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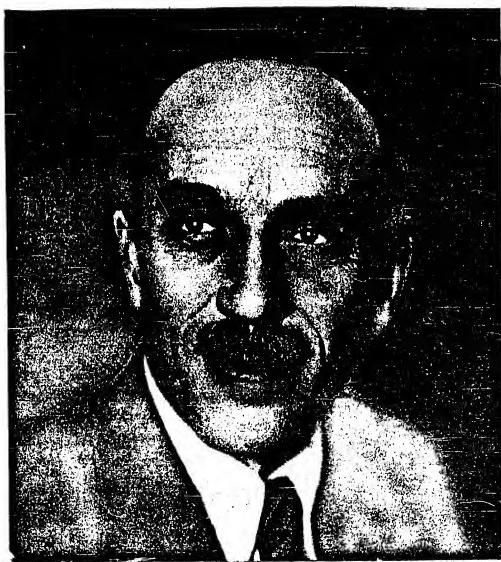
April

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To NIKOLAI NIKOLAEVICH SEMENOV

Dear Nikolai Nikolaevich:

The Division of Chemical Sciences of the Academy of Sciences of the USSR and the Editorial Board of the Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences, warmly congratulate you on the attainment of the age of sixty and the completion of forty years of scientific, pedagogical, and organizational activities.

Your name will always be associated with outstanding discoveries relating to chemical chain reactions and to the processes occurring during combustion, explosion and flame propagation. In your person, we salute also one who has long served as the Director of a leading Institute of the Division, the Institute of Chemical Physics of the Academy of Sciences of the USSR - a position in which you have shown outstanding initiative.

We hope, dear Nikolai Nikolaevich, that further great successes lie before you in all fields of your activity, and we wish you health and vigor in your creative labors.

Division of Chemical Sciences of the
Academy of Sciences of the USSR
and
Editorial Board of the Bulletin of
the Academy of Sciences of the USSR,
Division of Chemical Sciences

KINETICS OF THE OXIDATION OF ACETALDEHYDE BY PEROXYACETIC ACID

R. F. Vasilyev and N. M. Emanuel

Processes of oxidation with molecular oxygen belong to a class of chemical reactions that have a complicated mechanism. It was for this class of reactions that A. N. Bakh and K. Engler developed, in a particularly clear form, the concept of the important parts played by intermediate products and stages in chemical transformations. A new stage in the development of the theory of oxidative processes is associated with the introduction of the concept of a chain mechanism in these reactions. N. N. Semenov formulated the theory of degenerate branching, according to which peroxy compounds formed in the course of the reaction break down from time to time into radicals, which initiate new oxidation chains. This theory enables us to understand the slowness and autoacceleration of reactions between organic substances and molecular oxygen.

There can be no doubt that the direct oxidation of the substance by a peroxy compound, i. e., by combined oxygen, is also worthy of attention. Such processes can occur both in systems in which oxidation by molecular oxygen is proceeding and the peroxy compound is formed as an intermediary, and also in systems in which molecular oxygen is absent. The elucidation of the kinetics and mechanisms of processes of this kind presents much scientific and practical interest.

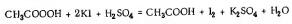
This paper is concerned with a study of the kinetics of the oxidation of acetaldehyde by peroxyacetic acid. In our choice of subject for investigation we were guided by the following considerations: a) reaction between an aldehyde and a peroxy acid is known to be one of the stages in the complex process of the oxidation of an aldehyde by molecular oxygen; b) the system aldehyde-peroxy acid is in itself a convenient model for the study of the kinetics and mechanism of oxidation by combined oxygen, for this process occurs comparatively readily and the number of reactants and products is small.

EXPERIMENTAL

Peroxyacetic acid was prepared from highly concentrated hydrogen peroxide and acetic anhydride by d'Ans and Frey's method [1]. The peroxyacetic acid content of the product was 70-82%, the remainder being acetic acid. It was kept at the temperature of dry ice (-78°) in a vessel having a ground-in stopper. It was shown that, when kept in this way, peroxyacetic acid does not undergo appreciable decomposition in the course of several months. The acetaldehyde solution was prepared from commercial acetaldehyde, which was dried over calcium chloride and distilled in a current of nitrogen into a vessel containing solvent. A freshly prepared solution was used on each occasion. Solvents were first distilled twice through a fractionation column. The cylindrical reaction vessels (diameter 15 mm, height 140 mm) were provided with ground-in stoppers and side arms through which nitrogen was passed in order to provide an inert atmosphere. In the temperature range 0° to -40°, a Dewar vessel containing acetone cooled with small portions of dry ice was used as a thermostat, constancy of temperature being maintained within ±0.3°. In the range 15-40°, a Hepple ultrathermostat, constant within ±0.03°, was used, and for experiments at 0° the reaction vessel was immersed in a Dewar vessel filled with melting ice.

Before a series of experiments, stock solutions of acetaldehyde and peroxyacetic acid were prepared. A definite amount (usually 10 ml) of the acetaldehyde solution was introduced into the reaction vessel immersed in the thermostat. When this solution had attained the temperature of the thermostat, a measured amount (usually 1-2 ml) of the peroxyacetic acid solution, also brought to the temperature of the thermostat, was added. The moment at which mixing occurred was taken as the beginning of the reaction. Tests for chemical analysis were taken with a 0.36 ml thin-walled pipet. The concentration of peroxyacetic acid and peroxy product was determined by Kagan and Lyubansky's method. Acetaldehyde was determined by titration of the hydrochloric acid liberated when the aldehyde reacted with hydroxylamine hydrochloride. A special method was developed for determining the acetic acid concentration. Experiments with artificial mixtures showed that, if the test samples were diluted with water, oxidation of aldehyde by peroxy acid continued during the analysis, and the values obtained for the acetic acid concentration were too high. We therefore diluted the test samples with potassium iodide solution. The peroxy acid was then immediately destroyed with liberation of iodine, and oxidation of the aldehyde was stopped. A definite volume of standard sulfuric acid was then added from a microburet, and iodine was titrated with thiosulfate solution. The total amount of acid was then titrated with phenolphthalein with alkali.

From the equation of the analytical reaction



and from the condition that the total amount of acid must be equal to the amount of alkali required in the titration, it is easy to determine the amount of acetic acid removed from the reaction vessel:

$$(\text{CH}_3\text{COOH}) = (\text{OH}^-)_{\text{titr}} - (\text{H}_2\text{SO}_4) + (\text{CH}_3\text{COOH})$$

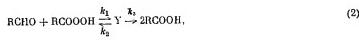
In which (CH_3COOH) is the amount of acetic acid in the sample, $(\text{OH}^-)_{\text{titr}}$ is the amount of alkali required in the titration, and (H_2SO_4) is the amount of peroxoacetic acid in the sample (all amounts are expressed in volumes of solutions of identical normality).

Theoretical and Experimental Kinetic Laws of the Reaction

It is known that the oxidation of aldehydes by peroxy acids results in the formation of carboxylic acids:

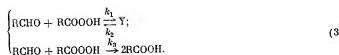


Several workers (Kagan and Lyubarik [2, 3], Bawn and Williamson [4], Meerwein and Bodendorf [5]) who have studied these reactions, have shown that in the course of the oxidation process a new peroxy compound is formed and then disappears again, this compound being in equilibrium with the original reactants. Treating this compound as an intermediate product, they assumed the following scheme of reaction:



in which Y is the intermediate peroxy compounds, and k_1 , k_2 , and k_3 are rate constants.

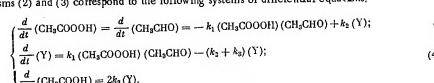
However, the observed behavior of the peroxy compounds cannot in itself serve as an unequivocal proof of the mechanism (2). The formation and subsequent decomposition of the new compound can be explained on the basis of a completely different mechanism; in which the acid is formed directly from the aldehyde and peroxy acid and the new peroxy compound is not an intermediary, but a by-product:



This second possibility was not envisaged by the authors of these papers, although their experimental data agreed equally well with both of the mechanisms (2) and (3). Hence, the very likely hypothesis of a stagewise mechanism for the process was not provided with the necessary experimental proof.

However, the mechanisms (2) and (3) differ fundamentally, and it would be expected that the kinetics of the process would also be different. We have examined theoretically the character of the kinetic laws corresponding to the mechanisms (2) and (3) in order to distinguish features that would make it possible to make a choice between these two alternative reaction schemes. The simplest method for making such an examination consisted in assuming reaction laws of a simple type (first and second order) for the kinetics of the separate stages. Comparison of the results of the theoretical analysis with experiment fully justifies this assumption.

The mechanisms (2) and (3) correspond to the following systems of differential equations:



$$\begin{cases} \frac{d}{dt} (\text{CH}_3\text{COOH}) = \frac{d}{dt} (\text{CH}_3\text{CHO}) = -(k_1 + k_2) (\text{CH}_3\text{CHO}) (\text{CH}_3\text{COOH}) + k_3 (\text{Y}); \\ \frac{d}{dt} (\text{Y}) = k_1 (\text{CH}_3\text{COOH}) (\text{CH}_3\text{CHO}) - k_2 (\text{Y}); \\ \frac{d}{dt} (\text{CH}_3\text{COOH}) = 2k_3 (\text{CH}_3\text{COOH}) (\text{CH}_3\text{CHO}). \end{cases} \quad (5)$$

We could not obtain exact solutions of these equations because they are not linear. An approximate solution can be obtained on the assumption that one of the reactants (aldehyde) is in excess with respect to the other (peroxy acid). The equations then reduce to linear forms, and solutions are obtained as follows:

a) in the case of mechanism (2)

$$x = \frac{1}{m_2 - m_1} \left\{ (m_2 - x) e^{-m_1 t} - (m_1 - x) e^{-m_2 t} \right\}, \quad (6)$$

$$y = \frac{x}{m_2 - m_1} (e^{-m_1 t} - e^{-m_2 t}), \quad (7)$$

$$z = 1 - \frac{1}{m_2 - m_1} \left\{ m_2 e^{-m_1 t} - m_1 e^{-m_2 t} \right\}, \quad (8)$$

b) in the case of mechanism (3)

$$x = \frac{1}{l_2 - l_1} \left\{ (1 - l_1) e^{-l_1 t} - (1 - l_2) e^{-l_2 t} \right\}, \quad (9)$$

$$y = \frac{x}{l_2 - l_1} (e^{-l_1 t} - e^{-l_2 t}), \quad (10)$$

$$z = 1 - \frac{1}{l_2 - l_1} \left\{ (l_2 - \gamma) e^{-l_2 t} - (l_1 - \gamma) e^{-l_1 t} \right\}, \quad (11)$$

in which x , y , and z are concentrations of components relative to the initial concentration of peroxyacetic acid;

$$x = \frac{(\text{CH}_3\text{COOH})}{(\text{CH}_3\text{COOH})_0}; \quad y = \frac{(\text{Y})}{(\text{CH}_3\text{COOH})_0}; \quad z = \frac{(\text{CH}_3\text{COOH})}{2(\text{CH}_3\text{COOH})_0}; \quad (12)$$

the values of α , β , γ , and τ are defined by the expressions:

$$\alpha = -\frac{k_1}{k_2} (\text{CH}_3\text{CHO})_0; \quad \beta = \frac{k_2}{k_3}; \quad \gamma = \frac{k_3}{k_2} (\text{CH}_3\text{CHO})_0; \quad \tau = k_3 t; \quad (13)$$

$-m_1 - m_2 = i_1$, and $-i_2$ are roots of the characteristic equations:

$$m_2 + (1 + \alpha + \beta)m_1 + \alpha\beta = 0 \text{ and } i^2 + (1 + \alpha + \gamma)i + \gamma = 0.$$

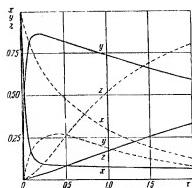


Fig. 1. Theoretical kinetic curves corresponding to the mechanism (2) constructed according to Equations 6, 7, and 8; x , y , and z are the relative concentrations of peroxyacetic acid, intermediate peroxy compound, and acetic acid, respectively. The curves are plotted for the following values of the parameters: $\alpha = 10$, $\beta = 0.1$; $\gamma = 1$; $\alpha = 1$, $\beta = 1$.

By way of example, Figures 1 and 2 give the theoretical kinetic curves plotted according to Equations 6-8 and 9-11 respectively, definite values being taken for the parameters α , β , and γ [i.e. so that definite relationships exist between the constants k_1 , k_2 , and k_3 and the concentration $(CH_3CHO)_0$]. As will be seen from Figures 1 and 2, the kinetic curves for peroxyacetic acid and the peroxy intermediate or by-product are qualitatively alike in the two cases. A qualitative difference in the form of the kinetic curves is found only for the final product, acetic acid. In the case of the mechanism (3) the acid accumulates according to a curve of a simple type, but in the case of the stagewise mechanism (2) the kinetic curve for the final product has an autocatalytic form. As can be readily shown by calculation, the inflection on the curve occurs at the point at which not more than 26% conversion has been attained.

The curves for the accumulation of acid coincide with the kinetic curves for the fall in the overall amount of active oxygen, i.e., the oxygen present both in the form of peroxy acid and peroxy intermediate or by-product, as follows from the general balance of the reactions in the stoichiometric equations (2) and (3). A comparison of the kinetic curves in Figures 1 and 2 leads to the conclusion that a choice between the mechanisms (2) and (3) can be made only on the basis of a study of the kinetics of the formation of acetic acid or the kinetics of the overall loss of active oxygen.

It is interesting to note that in investigations devoted to the oxidation of aldehydes by peroxy acids, the kinetics of acid formation have received practically no study. The paper of Bawn and Williamson [4] gives data on the overall loss of active oxygen in the reaction between acetraldehyde and peroxyacetic acid. The authors favor the concept of an intermediate stage [mechanism (2)]. Unfortunately, the number of experimental points is not sufficient for the course of the curve to be followed in detail, and the overall loss of active oxygen is represented by a curve of a simple type. Wittig and Pieper [5] studied the kinetics of the formation of benzoic acid and the consumption of peroxybenzoic acid in the oxidation of benzaldehyde. The kinetic curves given in the paper are of the simple type. However, the absence of experimental points on the kinetic curves makes it impossible for us to judge the accuracy to which the form of the curves was established. Thus, the experimental data presented by these authors corresponds more closely to the mechanism (3), in spite of the fact that they consider that the reaction proceeds by the stagewise mechanism (2).

Essentially, therefore, the question of the mechanism of the reaction and the part played in it by the

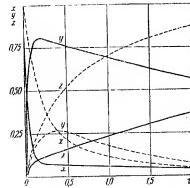


Fig. 2. Theoretical kinetic curves corresponding to the mechanism (3) constructed according to Equations 9, 10, and 11; x , y , and z are the relative concentrations of peroxyacetic acid, intermediate peroxy compound, and acetic acid, respectively. The curves are plotted for the following values of the parameters: $\alpha = 10$, $\gamma = 1$; $\alpha = 1$, $\beta = 1$.

peroxy compound formed during the reaction remains unsolved. We have therefore made a special study of the kinetics of the formation of acetic acid. The experiments were carried out in toluene solution at close to room temperature. Most of the experiments were carried out with an 8- to 15-fold excess of aldehyde with respect to peroxy acid, i.e. under the conditions under which Equations 6-11 are valid.

Figures 3 and 4 give the results of our study of the kinetics of the formation of acetic acid and the kinetics of the diminution in the sum of the concentrations of peroxyacetic acid and the peroxy product (i.e., in the overall concentration of active oxygen). It will be seen from these curves that the experimental points characterizing the two relationships are almost in coincidence. This coincidence of the two relationships enables us to use two sets of experimental data obtained independently of one another for the construction of a single kinetic curve, so that the form of this curve can be established with greater accuracy.

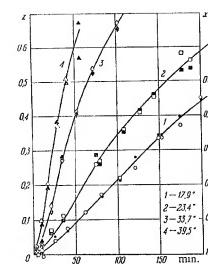


Fig. 3. Kinetics of the formation of acid (left scale, black points) and of the diminution in overall concentration of peroxy compounds (right scale, white points) in toluene solution. Initial concentrations: aldehyde 1.29 moles/liter, peroxy acid 0.10 mole/liter. Curves plotted from Equation 8.

As will be seen from Fig. 4, the formation of acetic acid proceeds with initial acceleration. A qualitative examination of the curves for the formation of acid therefore supports the mechanism (2). The curves in Figures 3 and 4 were plotted from Equation 8, being fitted to the experimental points by suitable choice of the parameters α , β , and k_2 . Calculation of k_2 was based on a simple transformation of the kinetic curves by a change in the scale of the time axis. The parameter k_2 , therefore, does not affect the form of the curve. The parameter $\alpha = \frac{k_1}{k_2} (CH_3CHO)_0 = \frac{(CH_3CHO)_0}{K}$ depends on the initial acetraldehyde concentration and the value of the equilibrium constant. The latter was determined in independent experiments (see below). The parameter α , therefore, was known beforehand. The parameter β was found by selecting a value that resulted in satisfactory fitting of the theoretical curve to the experimental points.

Table 1 gives the values of the parameters for the four experiments of this series, which were carried out at different temperatures.

The data in Table 1 in conjunction with Equation 7 can be used also for the construction of theoretical

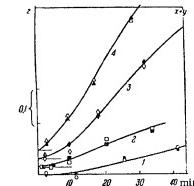


Fig. 4. Initial sections of the kinetic curves in Fig. 3. The curves have been displaced to different extents along the axis of ordinates; the scale for the measurement of degree of conversion is indicated. The numbering and signs correspond to Fig. 3.

Experiment No.	Temperature °C	α	β	$k_2 \cdot 10^4$ (sec⁻¹)
1	17.9	12.0	0.6	0.99
2	23.4	9.8	0.8	1.1
3	33.7	7.1	0.9	2.6
4	39.5	5.8	1.1	3.8

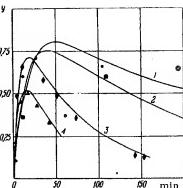


Fig. 5. Theoretical kinetic curves for the intermediate product, plotted from Equation 7 with the parameters given in Table 1. The points on the curves are the results of determinations of the concentration of intermediate product; they were not used for the construction of the curves. The numbering and signs correspond to Figures 3 and 4.

found in this way for a given series of experiments are closely in accord with the Arrhenius law $k = ae^{-E/RT}$, but they vary from series to series. Unsatisfactory reproducibility of the values of rate constants has been noted by other workers on oxidation by peroxy acids [7]. In particular, the reaction of acid formation is sometimes retarded to such extent that only the first stage is realized for practical purposes. The preexponential factor is less by a factor of several powers of ten than the usual values of about 10^{11} liter/mole-second or 10^9 second $^{-1}$ ($a_1 \sim 10^7$ liter/mole-second, $a_2 \sim 10^7$ – 10^8 second $^{-1}$, and $a_3 \sim 10^8$ second $^{-1}$), so that they cannot be treated within the framework of the usual collision theory for bimolecular reactions or in terms of bond-vibration frequencies in the case of unimolecular reactions. Moreover, the activation energies of the individual stages ($E_1 \sim 7$, $E_2 \sim 13$, $E_3 \sim 17$ kcal/mole) are very much less than the values characteristic for reactions between saturated molecules (several tens of kilocalories [8]).

The detailed mechanism of the reaction studied is probably more complex than that indicated in the overall scheme (2). It is possible that a chain reaction occurs. The experimentally determined rate constants may then be related in a complex manner with the constants for the elementary processes. For this reason, both the preexponential factors and the activation energies, which are combinations of the corresponding characteristics of the elementary stages, may differ substantially from the usual values *.

It must again be emphasized, however, that the chemical mechanism (2) closely represents the kinetics of the overall reaction and leads to conclusions that are in accord with the laws found experimentally. These laws are as follows:

1. The kinetics of the formation of acetic acid and the diminution in total active oxygen are described by Equation 8, the point of inflection occurring at about 25% conversion.

2. The concentration of the intermediate product varies with time in accordance with Equation 7. The fact that suitable treatment of data on the kinetics of formation of the final product enables to calculate correctly

curves for the intermediate product. These curves are shown in Fig. 5. The points distributed along the curves represent the results of special determinations of the concentration of the intermediate product in the respective experiments; they were not used for the construction of the curves. In all cases the fitting of the experimental points to the theoretical curves is quite satisfactory. This result provides a quantitative proof of the correctness of the mechanism (2).

Thus, the qualitative form of the kinetic curve for the formation of acid (initial acceleration), the close fit of the experimental points to the theoretical curves, and the possibility of calculating the changing concentrations of the intermediary from the kinetics of the formation of the final product have enabled us to solve the problem of the reaction mechanism. It can be considered to be established that the oxidation of acetaldehyde by peroxyacetic acid proceeds in stages via the formation and subsequent decomposition of an intermediate peroxy compound; i.e., that it proceeds in accordance with the mechanism (2). By the use of the parameters given in Table 1 and Equations 13, the rate constants k_1 and k_2 can be evaluated at each temperature. The rate constants

TABLE 2

Temp. (°C)	Concentration* (mole/liter)			K (mole/liter)
	(CH ₃ CO) ₂ O ₂	(CH ₃ COOOH) ₂	(CH ₃ COOOH) ₂ O	
-20	0.0948	0.0313	0.0013	0.098
-20	0.330	0.438	0.030	0.052
0.0	0.281	0.370	0.0060	0.052
0.0	0.330	0.0475	0.0072	0.052
0.0	0.330	0.0136	0.0070	0.061
+19.3	0.281	0.370	0.0122	0.128
+19.3	0.281	0.370	0.0122	0.113
+20.1	0.330	0.0475	0.0139	0.122
+20.4	0.330	0.0496	0.0165	0.187

* The values of concentration correspond to 20°. In the calculations the dependence of the density of toluene on temperature was taken into account.

ly the kinetic curves for the intermediate product shows that we may exclude the possibility that this peroxy compound is actually a by-product and that the initial acceleration in the kinetic curve for the acid is due to the complex mechanism by which it is formed from the original reactants. It will be clear that, if this were true, there would be no correlation between the two processes indicated above.

3. The rate constants obey the Arrhenius law, and the temperature coefficient for the formation of acid is greater than that for the formation of the intermediate peroxy compound. Experiment shows that there is a powerful temperature effect associated with the retardation of the second stage. Thus, at low temperatures (-40 – 0 °) practically no acetic acid is formed, and the reaction consists only in the establishment of the equilibrium:

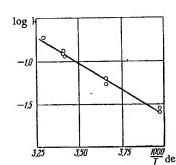


Fig. 6. Equilibrium constant for the formation of intermediate product as a function of temperature.

which the stage of acetic acid formation was retarded. The experiments were carried out in toluene solution,

Table 2 gives the data for, and the results of, the calculation of equilibrium constants from the formula:

4. The rate of formation of the intermediate product is proportional to the product of the concentrations of peroxy acid and aldehyde. That the reaction is of first order with respect to the peroxy acid follows from the applicability of Equations 6–8 in the description of the kinetics of the process. As the aldehyde was in excess in the above-described series of experiments, special experiments were carried out at lower concentrations. When the acetaldehyde concentration was changed by a factor of six, the bimolecular constant k_1 changed by only 6%, which indicated a first-order reaction with respect to aldehyde concentration. It is probable that, in this reaction, we are dealing with a complex process that simulates a simple one having simple kinetic laws.

We also obtained confirmation of the suggestion made by other authors [2–4] that an equilibrium exists between the intermediate peroxy compound and the original reactants. The equilibrium constant was determined in those experiments in

* There is another possible cause for the low value of the preexponential factor for the reaction resulting in the formation of the intermediate product – the low steric factor (10^{-3} – 10^{-5}) associated with addition reactions.

$$K = \frac{k_2}{k_1} = \frac{(CH_3CHO)_0(CH_3COOOH)_0}{(Y)_0} = \frac{(CH_3CHO)_0 - (CH_3COOOH)_0 + (CH_3COOOH)_0}{(CH_3COOOH)_0 - (CH_3COOOH)_0}$$

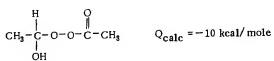
in which ($_0$) indicates initial concentrations and ($_0$) indicates final concentrations (at the equilibrium state).

A linear relationship is found between the logarithm of the equilibrium constant and the reciprocal of the temperature (Fig. 6), and this permits us to write the following expression for the equilibrium constant:

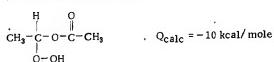
$$K = 1.6 \cdot 10^3 \cdot e^{-\frac{RT}{1000}}$$

The formation of the intermediate product is therefore accompanied by the evolution of 5.5 kcal/mole. Estimates of heat of reaction on the basis of mean bond energies give the following values for structures suggested in the literature for the intermediate peroxy compound:

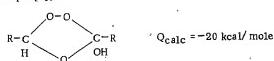
I. 1-Hydroxyethyl peroxyacetate (Wieland [9], Kagan and Lyubarsky [2, 3]):



II. 1-Hydroperoxyethyl acetate (Bawn and Williamson [4]):



III. An isoozonide (Wittig and Pieper [8]):



The error in such a calculation is of course large, and it may therefore be considered that the experimental value is in accord with the theoretical estimate.

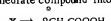
SUMMARY

1. On a basis of a comparison of the theoretical and experimental kinetic laws it was shown that the oxidation of acetaldehyde by peroxyacetic acid proceeds in two stages:

a) reversible formation of an intermediate peroxy compound:



b) decomposition of the intermediate compound into the final product, acetic acid:



2. A study was made of the equilibrium of the reversible reaction resulting in the formation of the intermediate product, and it was shown that the reaction is exothermic, the heat of reaction being 5.5 kcal/mole.

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SPECTROSCOPIC STUDY OF THE INTERMEDIATE PRODUCT AND
INTERMEDIATE STAGE OF REACTION IN THE OXIDATION
OF ACETALDEHYDE BY PEROXYACETIC ACID
R. F. Vasil'yev, A. N. Terenin, and N. M. Emanuel

Physical methods of investigation have not yet received adequate application in the study of the processes of liquid-phase oxidation by molecular oxygen, and they have not been applied in the study of oxidation by peroxy compounds (i.e., one of the stages in the process of oxidation by molecular oxygen). However, the chemical analysis and identification of individual peroxy compounds taking part in these processes, which have complex mechanisms, comprise a difficult problem that cannot always be solved. There can be no doubt that in this fact lies one of the causes of the inadequate study given to the chemistry of oxidation processes. It is not surprising, therefore, that papers should appear relating to investigations having the object of developing physical methods for the analysis and identification of peroxy compounds, e.g., spectroscopic [1-3] and polarographic [4] methods. It was with this object that systematic studies recently began to be made of various peroxy compounds. Infrared spectra were determined for some dozens of peroxy compounds of various classes [1, 2, 5, 8, 9]. The results obtained were applied in the study of the photochemical [9, 10] and thermal [3] oxidation of aldehydes by molecular oxygen, and in these processes intermediate products - peroxy acids - were detected, and the kinetics of their formation and further transformation were studied.

In the spectra of all of the peroxy compounds absorption bands were found in the frequency range 800-900 cm^{-1} . These bands were ascribed to the valency vibrations of the peroxide linkage $\text{O}-\text{O}-$. Theoretically, such an assignment is not well founded, for the vibration at a peroxide linkage is not characteristic [2, 8, 11]. Moreover, other vibrations may also appear in this range (deformational vibrations of the CH_3 group, vibrations of the molecule as a whole, etc.). Actually, it is found that a few bands in the 800-900 cm^{-1} region occur in the spectra of many peroxy acids.

As these bands are present in the spectra of all peroxy compounds investigated up to the present time, it appears that the presence of an absorption band in the 800-900 cm^{-1} region is a distinguishing feature for peroxy compounds. In the vibration corresponding to this band, not only the $\text{O}-\text{O}-$ link takes part but also neighboring linkages. The position of the absorption band therefore varies (over a range of 100-120 cm^{-1}) according to the structure of the peroxy compound.

We have examined the possibility of applying the spectroscopic method for the study of processes of oxidation by peroxy compounds. As subject for study we selected the oxidation of acetaldehyde by peroxyacetic acid. In so doing we were guided by the following considerations:

- a) reaction between aldehydes and peroxy acids is known to be one of the stages in the complex process of the oxidation of aldehydes by molecular oxygen;
- b) as a result of work by Soviet and foreign investigators [12-14] it has been established that the reaction selected proceeds stagewise via intermediate formation and subsequent decomposition of an intermediate peroxy compound (Y);



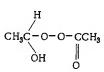
- c) the infrared spectra of the original reactants and the final products are comparatively simple and

are well known in the literature.

Peculiar interest was presented by a study of the intermediate stage and intermediate reaction product with the aid of infrared spectroscopy. In its relation to this study, the difference in the position of the —O—O— absorption band in different compounds was regarded by us as a favorable circumstance, since such a difference might insure satisfactory spectroscopic detection of the intermediate peroxy compound in presence of the original peroxy acid. We may point out that the solution of such a problem by chemical methods is often impossible, since the original and intermediate peroxy compound generally have identical chemical properties. Hence, the possibility cannot be excluded that many reactions of this kind that are regarded as simple are in fact processes that proceed in stages.

Kinetic experiments have established that the intermediate peroxy compound is an equimolecular addition product of acetdehyde and peroxyacetic acid [12-14]. Structural formulas have been proposed in the literature for this compound:

1) 1-Hydroxyethyl proxacetate [12]:



2) 1-Hydroperoxyethyl acetate [13]:



3) An isoazonide [15]:



No proof has been advanced for any of these possible structures by the authors who postulated them.

Since the intermediate product is a peroxy compound, it was natural to seek its spectral characteristics in the region of the frequencies of the —O—O— link ($800-900 \text{ cm}^{-1}$). As solvent we selected nitromethane, which has a strong but narrow absorption band at 920 cm^{-1} and some other very weak bands in this region. The spectra were determined on an IKS-11 infrared spectrometer having a rock salt prism. The solutions were held in a cell having rock salt windows or in a special cell having polyethylene windows; the latter is the more convenient in work with solutions of such a corrosive substance as peroxyacetic acid. The work was carried out in two stages: preparation of the intermediate product, and the determination of its spectrum. The method of preparing the intermediate product is described in the literature [16]. When toluene solutions of acetdehyde and peroxyacetic acid are mixed and the mixture is placed in a cryostat, after several hours at -40° to -50° crystals of the intermediate peroxy compound are precipitated (m.p. -19° to -20°). This process is extremely sensitive to variations from optimum concentrations and to impurities (in particular, water). We carried out this preparation, poured the mother liquor from the precipitate, and dried the crystals with the aid of ether. We then dissolved part of the product in nitromethane, filled a cell with the solution, and determined its spectrum. All possible measures were taken to keep the solution at room temperature for as short a time as possible: a portion of the precipitate was dissolved in cooled solvent, the test sample was taken in a cooled pipet, and the time taken to determine the spectrum was confined to a few minutes.

The results are presented in Fig. 1. In the spectrum of the solution of the precipitate powerful absorption is to be clearly observed at a wave number of 847 cm^{-1} , at a place in which the original reactants and final products (acetdehyde, peroxyacetic acid, and acetic acid) do not have absorption bands. The new

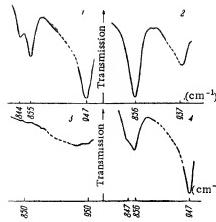


Fig. 1. Spectra of solutions of original reactants, final product, and reacting mixture in the region of the valency vibrations of the —O—O— link: 1) acetdehyde (0.6 mole/liter); 2) peroxyacetic acid (1.9 moles/liter); 3) acetic acid (1.5 moles/liter); 4) reacting mixture. Thickness of absorbing layer 0.1 mm. Solvent, nitromethane. The broken line indicates the region of the absorption of the solvent.

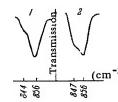


Fig. 2. Summation spectrum of solutions of acetdehyde and peroxyacetic acid in nitromethane (1), and the spectrum of the reacting mixture (2) (in the region of the valency vibrations of the —O—O— link). Solvent - nitromethane. Thickness of absorbing layer - 0.2 mm, Concentration of solution - 0.7 moles/liter.



* Data in the literature give convincing support to this view. Karyakin and Nikitin [1] observed only small displacements of bands in the region $800-900 \text{ cm}^{-1}$ in a series of cyclic hydroperoxides, but could not distinguish bands that preserved their position in a series of peroxides. According to Minkov's results [2] on the spectra of about thirty peroxides and hydroperoxides, the most intensive bands are distributed as follows: in the spectra of peroxides - in the range $820-890 \text{ cm}^{-1}$; in the spectra of hydroperoxides - in the much narrower range $835-855 \text{ cm}^{-1}$.

band partially overlaps the absorption bands of peroxyacetic acid and acetdehyde (wave number of both of these bands: 856 cm^{-1}) resulting in a characteristic contour having an inflection. When the spectrum is determined on samples that have been kept for 20-30 minutes at room temperature (in the course of this time the intermediate product disappears, being decomposed into acetic acid), the 847 cm^{-1} absorption band is no longer present. This indicates that the new absorption band is definitely not due to foreign substances (such as ether and toluene).

The band of the intermediate product at 847 cm^{-1} was found also in the spectrum obtained when the reaction was carried out directly in nitromethane (without isolation of the crystals). This spectrum is given in Fig. 2. This figure shows also the summation spectrum of acetdehyde and peroxy acid solution. Both spectra were determined in a double cell. Comparison of the spectra shows that the appearance of the 847 cm^{-1} band cannot be explained as the result of the superposition of the bands of the original reactants.

There can be no doubt that the band that we have found at 847 cm^{-1} is an absorption band of the intermediate peroxy compound. It is probably to be attributed to valency vibrations of the —O—O— link. The displacement by 9 cm^{-1} from the spectrum of peroxyacetic acid must be regarded as small when it is considered that the corresponding bands in the spectra of the peroxy compounds that have been investigated are distributed over a wide range ($100-120 \text{ cm}^{-1}$). This result indicates that the change in structure undergone by the molecule does not have a great effect on the dynamics and kinematics of the vibrations of the peroxy link. It may be assumed that this effect will be small when the intermediate product, like peroxyacetic acid, contains a hydroperoxy group, and will not be small when the hydroperoxy group is converted into peroxy (i.e., to peroxy linked to carbon at both sides) in the course of the reaction *.

In view of the spectroscopic results therefore, of the three structures proposed in the literature for the intermediate compound the most probable is that postulated by Bawn and Williamson - 1-hydroperoxyethyl acetate:

We did not succeed in determining the band of the intermediate product in the isolated state, since a considerable move toward equilibrium between it and the original reactants always occurred during its dissolution in nitroethane, so that acetaldehyde and peroxyacetic acid were always present in the solution.

The low intensity of the band and the overlapping of this band and that of peroxyacetic acid made it impossible to determine concentrations quantitatively by spectrum analysis. Nevertheless, from the spectrum of the reacting mixture we succeeded in following qualitatively the kinetics of the establishment of equilibrium between the original reactants and the intermediate peroxy compound and the kinetics of the reaction leading to the formation of acid.

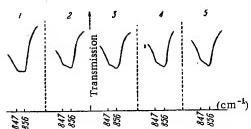


Fig. 3. Spectra of reacting mixture: 1) immediately after dissolution of crystals in nitroethane; 2) 11 minutes after dissolution; 3) after 23 minutes; 4) after 68 minutes; 5) after 73 minutes. Thickness of absorbing layer - 0.1 mm. Temperature - -10° .

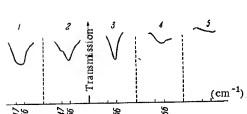


Fig. 4. Spectra of reacting mixture: 1) immediately after dissolution of intermediate product; 2) 9 minutes after dissolution; 3) after 22 minutes; 4) after 50 minutes; 5) after 80 minutes. Thickness of absorbing layer - 0.1 mm. Temperature - $+20^{\circ}$.

Figures 3 and 4 give the results of two experiments, carried out at -10° and $+20^{\circ}$ respectively. In both experiments the intermediate product, which separated in the form of crystals, was dissolved in nitroethane. The resulting solution was placed in a thermostat (-10° or $+20^{\circ}$), test samples were transferred to the cell, and the spectrum was recorded.

In experiments on the kinetics of the oxidation of acetaldehyde by peroxyacetic acid [14] it was established that the temperature coefficients for the reactions of formation of the intermediate product and its decomposition into the original reactants are less than the temperature coefficient for the reaction of formation

of acetic acid. For this reason, scarcely any acetic acid is formed at -10° , and reaction consists only in the establishment of equilibrium between the original reactants and the intermediate peroxy compound. Accordingly, the intensity of the band of the intermediate product (847 cm^{-1}) diminishes relative to that of the peroxyacetic acid band (856 cm^{-1}) and finally takes up a constant value (Fig. 3). At 20° establishment of equilibrium and decomposition of the intermediate product into acid proceed simultaneously, the first process being the more rapid so that the intensity of the band due to the intermediate product diminishes at first, and then also that due to peroxyacetic acid diminishes (Fig. 4).

Fig. 5 shows a series of spectrograms taken in succession over a wider range of frequencies. The solution from which the test samples were taken was at room temperature. The gradual disappearance of the absorption bands of peroxyacetic acid (856 cm^{-1}), the intermediate product (847 cm^{-1}), and acetaldehyde (947 cm^{-1}) can be clearly seen.

SUMMARY

1. The intermediate product formed in the oxidation of acetaldehyde by peroxyacetic acid was isolated in the form of crystals. A band at 847 cm^{-1} was found in the absorption spectrum of its solution, and this was ascribed to the vibration of the peroxy link in the molecule of the intermediate product.

2. The variation of the spectrum of the reacting mixture with time is in full accord with a stagewise reaction mechanism. The presence of an intermediate stage and an intermediate product is quite clearly manifest in the spectrum - a fact that indicates that the application of infrared spectroscopy to the study of oxidation by peroxy compounds forms a promising line of attack on this problem.

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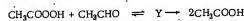
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EFFECT OF SOLVENTS ON THE RATE OF OXIDATION OF ACETALDEHYDE
BY PEROXYACETIC ACID FROM THE POINT OF VIEW OF
INTERMOLECULAR HYDROGEN BONDING

R. F. Vasilyev, A. N. Terenin, and N. M. Emanuel

Whenever a study is made of the kinetics of a reaction in solution, the question of the effect of the solvent on the rate and mechanism of the process is bound to arise. It then becomes important to determine how the observed effect of the solvent arises.

We have carried out experiments on the kinetics of the oxidation of acetaldehyde by peroxyacetic acid in eight different solvents: carbon tetrachloride, chloroform, toluene, benzene, nitrobenzene, methanol, nitromethane, and acetone. The reaction between peroxyacetic acid and acetaldehyde results in the formation of acetic acid, and it occurs in stages via the reversible formation and subsequent decomposition of an intermediate peroxy compound Y [1]:



With the object of obtaining reproducible results, we adopted the procedure of diluting stock solutions with solvents. As stock solutions we prepared solutions of peroxyacetic acid and acetaldehyde in toluene. At the beginning of an experiment 1.5 ml of the aldehyde stock solution was diluted with 10 ml of solvent, and 0.5 ml of peroxy acid stock solution was then mixed in. Hence, all of the experiments were carried out with the same solvents, and the solvent whose effect was being studied comprised about 84% of the volume of the reacting mixture. This procedure made it possible to compare quantitatively the rates of the process in various solvents. Kinetic measurements were made for dilution in the amounts of peroxyacetic acid and in total active oxygen, i.e., the active oxygen present both as peroxyacetic acid and as intermediate product. Stoichiometric considerations show that the latter kinetic relationship is identical with the kinetics of acetic acid formation.

The experimental results are shown in Fig. 1, from which it will be seen that the rate at which peroxyacetic acid is used up is identical in chloroform, toluene, benzene, and nitrobenzene; the rate is somewhat higher in carbon tetrachloride. In all of these solvents the formation of the intermediate peroxy compound proceeds to approximately the same degree of transformation, namely 70-78%. The rate at which the intermediate peroxy compound is formed in methanol, nitromethane, and acetone* is very much less than in the solvents of the first group.

In all of the solvents the two stages of the reaction are clearly marked. The solvents vary in their effects on the rates of the two stages. For example, the intermediate product is formed more slowly in methanol than in solvents of the first group, whereas the rate of the decomposition of the intermediate product into acid is higher in methanol than in any of the other solvents.

Our experimental results on the dependence of the course of the reaction on the identity of the solvent

* Special experiments showed that acetone is not oxidized by peroxyacetic acid at 24.2°.

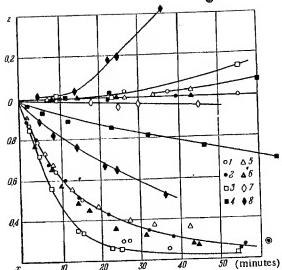


Fig. 1. Kinetics of the consumption of peroxyacetic acid (x) and the formation of ester (z) in various solvents at 24.2°: 1) in carbon tetrachloride; 2) in chloroform; 3) in toluene; 4) in benzene; 5) in nitrobenzene; 6) in methanol; 7) in nitromethane; 8) in acetone. Initial concentrations: peroxyacetic acid 0.273 mole/liter; acetaldehyde 0.216 mole/liter.

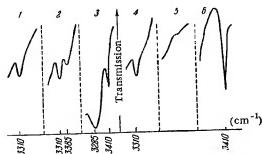


Fig. 2. Infrared spectra of peroxyacetic acid solutions (0.7 mole/liter): 1) in toluene; 2) in 1:1 mixture of toluene and nitromethane; 3) in 1:1 mixture of toluene and acetone; 4) in 1:1 mixture of toluene and nitrobenzene; 5) spectrum of pure nitromethane; 6) spectrum of pure acetone. Thickness of layer = 0.1 mm.

can be interpreted as follows. The molecular structure of the solvents in which the first stage of reaction is slow (methanol, acetone, nitromethane) is such that hydrogen bonding is possible between the solvent molecule and the molecule of peroxyacetic acid. A hydrogen bond can be formed between the hydroxyl group of the peroxyacid on the one hand and the hydroxyl, carbonyl, or nitro group of the solvent on the other. The possibility of the formation of a second hydrogen bond cannot be excluded, i.e., between the carbonyl group of the per-

oxy acid and the hydroxyl groups of the solvents. For the remaining solvents (with the exception of nitrobenzene) we may state before hand that the formation of such hydrogen bridges is impossible on account of the absence of suitable structural groups.

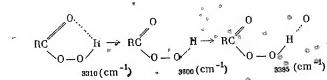
The presence of solvent molecules linked to reactant molecules by hydrogen bonds can affect reaction rate. The kinetic detection of a hydrogen bond was considered in investigations by one of us and coworkers [2, 3]. In these investigations it was established that in certain cases hydrogen bonding has a great effect on the kinetics of chemical reactions. In particular, it was found that it was possible to detect intramolecular hydrogen bonding by kinetic methods [4]. In our case, solvent molecules hydrogen-bonded to peroxyacetic acid molecules can reduce the accessibility of the latter to acetaldehyde molecules and so bring about a reduction in reaction rate.

As is well known, the most reliable method for establishing the presence of a hydrogen bond consists in a study of the vibration spectra (infrared and Raman) of suitable mixtures [5]. Hydrogen bonding causes a displacement and broadening in the bands of the H-Hs concerned in the hydrogen-bond formation. For example, the wave number of the vibrations of a hydroxyl in any compound is 3600-3750 cm⁻¹, which is reduced when the hydroxyl is hydrogen-bonded to 3000-3500 cm⁻¹, depending on the strength of the hydrogen bond. We studied the infrared absorption spectra of peroxyacetic acid solutions in the range 3000-3500 cm⁻¹. The infrared spectra were recorded with an IKS-11 infrared spectrometer having a lithium fluoride prism. The solvents used were equimolar mixtures of toluene with nitromethane, nitrobenzene, and acetone. The spectrum of a solution of the peroxy acid in methanol was not determined because the solvent itself absorbs strongly in this region of the spectrum owing to association due to hydrogen bonding. The spectra obtained are given in Fig. 2. In toluene solution in this region of the spectrum there is an absorption band at 3310 cm⁻¹, which must be attributed to an intramolecular hydrogen bond formed in molecules of aliphatic peroxy acids [6, 7]:



(the wave number of the "free", i.e., not hydrogen-bonded, hydroxyl is in this case 3600 cm⁻¹)

When nitromethane is added to a toluene solution of peroxyacetic acid, a new band (3385 cm⁻¹) appears which is present neither in the toluene spectrum nor in the nitromethane spectrum. We attribute this band to the vibrations of the hydroxyl group of the peroxy acid, which is hydrogen-bonded to the nitromethane molecule. We consider that in some of the peroxy acid molecules the intramolecular hydrogen bond is broken and the "free" hydroxyl group attaches itself to an oxygen atom of nitromethane:



When acetone is added to a toluene solution of peroxyacetic acid, considerable changes occur in the spectrum: the band broadens and increases in intensity, and its maximum is displaced toward the long waves and takes up the position 3325 cm⁻¹. Since pure acetone does not absorb in this region it is natural to assume that the new absorption band is associated with a hydrogen bond between the acetone and peroxyacetic acid molecules:

The high intensity of the α -band - higher than in nitroethane solution - indicates that a larger number of molecules are hydrogen-bonded. It is possible that it is for this reason that the rate of reaction in acetone is lower than in the other solvents. The addition of nitroethane does not affect the spectrum of a solution in toluene, a fact that indicates that no hydrogen bonding occurs between nitroethane and peryoxyacetic acid. It is known that nitrobenzene, owing to its low basicity, does not form a strong hydrogen bond [8]. It should be noted that in nitrobenzene reaction proceeds at the same rate as in chloroform, toluene, and benzene, i.e., in the solvents that cannot be hydrogen-bonded to peryoxyacetic acid on account of the absence of suitable structural groups. There can be no doubt that a hydrogen bond is formed between methanol and peryoxyacetic acid, although we were unable to establish this directly.

Practically no work has been reported in the literature on the effect of solvents on the rate of oxidation by peroxy acids. Such data as exist, however, confirm our hypothesis concerning the effect of the hydrogen bond on the reaction. Meerwein and Bodegaer [9] studied the oxidation of propylbenzene and anisaldehyde by perbenzoic acid. It was found that the rates of these two reactions were considerably lower in ether, acetone, and ethanol than in nitrobenzene, chloroform, benzene, carbon tetrachloride, and cyclohexane. It will be seen that, if this case also, reaction is slower in solvents that form hydrogen bonds than in those that are unable to form hydrogen bonds. Jorissen and van der Beek [10, 11] found that only in an acetone solvent could they succeed in isolating hydroxybenzoic acid formed by the autoxidation of benzaldehyde; in other solvents it disappeared instantaneously owing to rapid reaction with benzaldehyde. According to Kagan and Lyubarsky [12], the rate of the oxidation of acetaldehyde by peroxyacetic acid is almost the same in benzene, chloroform, nitrobenzene, and toluene (i.e., in the solvents that do not form hydrogen bonds with peroxyacetic acid).

Thus, on the basis of the results obtained by us and by other workers we may conclude that the presence of 3 hydrogen bond has a definite effect on the rate of oxidation of acetaldehyde by peroxyacetic acid (more exactly, on the rate of the first stage of this reaction). This explains the difference in the kinetics in different solvents: retardation of reaction is associated with the blocking effect of solvent molecules hydrogen-bonded to peroxyacetic acid molecules.

SUMMARY

It was shown that retardation of reaction found in some solvents is due to the blocking effect of solvent molecules hydrogen-bonded to peroxyacetic acid molecules. The presence of hydrogen bonds between peroxyacetic acid molecules and solvent molecules (nitromethane, acetone) was established by the determination of infrared absorption spectra.

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KINETIC METHOD OF APPLYING LABELED ATOMS IN THE
INVESTIGATION OF COMPLEX CHEMICAL AND
BIOCHEMICAL PROCESSES

COMMUNICATION 6. RATES OF FORMATION AND TRANSFORMATION OF ACETALDEHYDE,
CARBON MONOXIDE, AND CARBON DIOXIDE IN THE OXIDATION OF PROPENE

M. B. Neiman, V. Ya. Efremov, N. K. Serdyuk, and A. F. Lukovnikov

In spite of the large number of investigations that have been devoted to the oxidation of hydrocarbons, the mechanism of this complex process has not yet been adequately studied. No unified view has been established even with respect to the basic features of the mechanism. Thus, some authors consider that the substance causing degenerate branching is a peroxy compound, and others that it is acet aldehyde. Some authors consider that acet aldehyde is simultaneously formed and consumed in the course of the reaction [1], and others consider that the consumption of acet aldehyde comes practically to a stop in the period when rapid oxidation of the hydrocarbon is occurring [2]. The question of the ways in which carbon oxides are formed and their rates of formation is also obscure. All of these questions have been investigated previously mainly by classical methods. As we considered that the kinetic method that we have developed could give some help in elucidation of these matters, we have now investigated the oxidation of propene by this method.

As we were interested primarily in the behavior of acet aldehyde, we decided to carry out experiments on oxidation in a propene-oxygen mixture to which a small amount of $\text{CH}_3\text{C}^4\text{H}_2\text{O}$ was added. Some series of experiments were also carried out with additions of $\text{C}^4\text{H}_2\text{O}$.

So that the kinetic method could be applied it was necessary first to develop a procedure for the determination of the acet aldehyde concentration in the oxidation products of propene, in which it was possible that some other aldehydes might be present. Also, it was necessary to determine whether hydrogen could be transferred from alcohols to acet aldehyde in accordance with the equation:

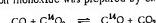


It will be seen that transfer of hydrogen atoms between alcohol and aldehyde could result in the formation of labeled alcohol from labeled aldehyde, which, if the kinetic method were applied, would distort the results of radiochemical analysis.

EXPERIMENTAL

Synthesis of Reactants, Experimental Conditions. Propene was prepared by dehydration of isopropyl alcohol over a catalyst. It was carefully purified. Mass-spectrometric analysis showed that our product did not contain more than 0.3% of butenes.

Labeled carbon monoxide was prepared by catalytic exchange in the reaction:



as described in the paper [3].

®

Acetaldehyde labeled with radioactive carbon in the carbonyl group was prepared as follows:



as described in the paper [4].

The experiments on the oxidation of propene were carried out in a glass vacuum apparatus. The volume of the reaction vessel was 295 ml, and its diameter was 4 cm.

The investigation by the kinetic method we isolated carbon oxides and acetaldehyde from the oxidation products. The concentrations and specific activities of these products were determined by methods described previously [3, 5].

Determination of the Acetaldehyde Content. In order to apply the kinetic method it was necessary to know the acetaldehyde concentration, not the total concentration of aldehydes. Since the higher aldehydes are reduced at the same potential as acetaldehyde, it was necessary to establish whether the reaction products included any higher aldehydes and whether other oxygen-containing products present affected the height of the polarographic wave for acetaldehyde.

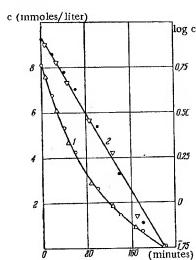


Fig. 1. Concentration of a standard acetaldehyde solution (0) and of a solution of the oxidation products of propene (y) as a function of the duration of passage of hydrogen (Curve 1); the same curve plotted in the coordinates $\log c$ and time (Curve 2)

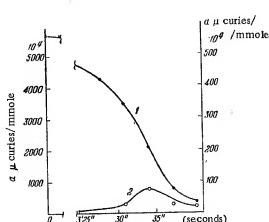


Fig. 2. Variation in specific activity: 1 - CO₂; 2 - CO₂

It has been established previously that, when hydrogen is blown through an aqueous solution of a volatile compound, the concentration of the latter varies according to the law

$$x = x_0 e^{-kt} \quad (1)$$

in which x is the concentration of the substance being blown out, x_0 is its initial concentration, t is the duration of blowing, and k is a constant. To a fairly close approximation, the constant k can be calculated from the formula:

$$k = \frac{\Delta \ln p}{1244V}, \quad (2)$$

in which A is the rate of blowing, p_0 is the vapor pressure of the substance investigated, V is the volume of the solution, and α is a coefficient characterizing the departure of the given solution from the ideal.

The value of k can be found also experimentally from the curve for the dependence of the concentration of the volatile compound on the duration of blowing with hydrogen. If we plot $x = f(t)$ [1] in the coordinates $\log x$ and t , k will be equal to the slope of the curve. For a complex mixture of compounds having various vapor pressures, the slope of the curve will vary and the value of k will be different.

It appeared to us, therefore, to be possible to decide whether any higher aldehydes were present in the mixture by comparison of the curves for the variation in concentration during the passage of hydrogen through a solution of pure acetaldehyde and through an actual mixture of the oxidation products of propene. Hydrogen was passed through an electrolytic vessel containing the solution of acetaldehyde or reaction products at a rate of 10.5 ml/minute at 22°. After a period of 20-60 minutes, blowing was discontinued and polarography was carried out in 0.1 N LiCl. The results of the experiments are presented in Fig. 1. The points corresponding to the acetaldehyde concentration in the solution of reaction products and in the standard acetaldehyde solution lie on a single curve. The coincidence of the curves indicates that higher aldehydes are substantially absent from the reaction products, and other oxygen-containing compounds do not affect the height of the polarographic wave for acetaldehyde. The same conclusion follows from a comparison of the values of the constant k calculated from Equation 2* and found from the slope of the straight line $\log x = f(t)$.

Study of the Possibility of Hydrogen Transfer in a Mixture of Alcohol and Acetaldehyde. In order to resolve this matter, an equimolecular mixture of CH₃CHO and CH₃C¹⁴H₅OH was heated in a glass vessel for several hours. The acetaldehyde was then analyzed radiochemically. Over the temperature range studied (315-337°) we did not detect any appreciable transfer of hydrogen from alcohol to acetaldehyde. The specific activity of acetaldehyde was about 3 conventional units irrespective of the duration of heating (the original specific activity of the alcohol was 500 units). It is possible that there was a slight amount of oxygen in the original mixture of alcohol and acetaldehyde, and this immediately oxidized CH₃C¹⁴H₅OH to CH₃C¹⁴HO and was then used up. When the mixture was heated further, the specific activity of the acetaldehyde did not change. In view of the minute extent, or even absence, of hydrogen transfer, we may neglect it.

Experimental Results

Oxidation of Propene in presence of C¹⁴O and CO₂. In order to establish the course of the process of CO₂ formation in the oxidation of propene and the proportion of it that is formed from CO₂, we carried out experiments on the oxidation of propene containing additions of C¹⁴O and CO₂. Oxidation was carried out in a mixture of 48% of C₂H₆, 50.7% of O₂, 1.08% of CO₂, and 0.22% of C¹⁴O at 340° and an initial pressure of 281 mm. The variation in the specific activities of CO and CO₂ in the course of the process is shown in Fig. 2. As can be seen from Fig. 2, the specific activity of carbon monoxide falls fairly rapidly, whereas that of carbon dioxide rises at first, passes through a maximum, and then falls off. If CO₂ were formed solely from CO, then at the maximum the specific activity curve for CO₂ would intersect the specific activity curve for CO. In our case the maximum α_{CO_2} lies considerably below the α_{CO} curve. This indicates that CO₂ is formed partially from CO, but mainly from other reaction products.

According to the equations for the kinetic method [3], the specific activities of CO and CO₂ and the rates of formation of CO₂ by parallel routes are related together at the point corresponding to maximum α_{CO_2}

* The value of $p_0\alpha$ was found from $p = p_0\alpha x$, in which p is the partial vapor pressure of acetaldehyde in an aqueous solution and x is its concentration. The dependence of p on x for acetaldehyde has been studied by Dobritsinsky [7].

by the equation:

$$\frac{w}{w_1} = \frac{\alpha_{CO}}{\alpha_{CO_2}} \quad (3)$$

In which w_1 is the rate of formation of CO_2 from carbon monoxide, and w is the overall rate of formation of CO_2 (by all routes).

It follows from our results that

$$\frac{\alpha_{CO}}{\alpha_{CO_2}} = 26.$$

This means that only 3-4% of carbon dioxide is formed by the oxidation of carbon monoxide. The bulk of it is formed in other ways.

These results are in accord with those obtained in an investigation of the behavior of CO and CO_2 in the butane oxidation [3] so that we may infer that there is a general mechanism for the formation of CO_2 which is common to the oxidation of saturated and unsaturated hydrocarbons.

Oxidation of Propene in presence of $CH_3C^{14}H_9O$. Experiments on the oxidation of propene in presence of $CH_3C^{14}H_9O$ were carried out with the mixture of 50% of O_2 , 48.87% of C_3H_8 and 1.13% of $CH_3C^{14}H_9O$, the initial pressure being 243 mm. and the temperature 315°. The kinetic curve, characterized by the occurrence of four cool flames, is shown in Fig. 3.

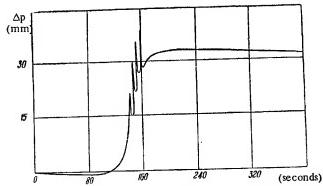


Fig. 3. Variation in pressure during the oxidation of propene
(P_0 243 mm; temperature 315°)

The curves for the variation in concentration and specific activity of acetaldehyde are presented in Fig. 4. It should be noted that the fall in the specific activity of acetaldehyde with time does not correspond to the rise in its concentration; the latter changes much more rapidly than the former. Thus, before the cool flames occur, the concentration has grown by a factor of 3.8, whereas the specific activity has fallen by a factor of 5.5. After the extinction of the cool flames, the concentration increases by a factor of 5.5 and the specific activity falls by a factor of 19.5. This indicates that acetaldehyde is being consumed as well as formed.

Discussion of Experimental Results

From a knowledge of the way in which the concentration and specific activity of acetaldehyde vary, we may calculate the rates at which it is formed and consumed. It is known [8] that

$$-\frac{d\alpha}{dt} = \frac{dw}{x}. \quad (4)$$

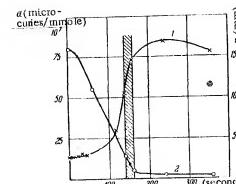


Fig. 4. Variation in concentration (Curve 1) and specific activity (Curve 2) of acetaldehyde (the shaded area corresponds to the cool-flame zone)

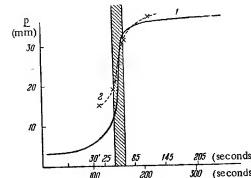


Fig. 5. Kinetics of the formation of acetaldehyde - no account being taken of its subsequent consumption (Curve 1). Curve 2 is constructed from Polyak and Shtern's data

in which α is the specific activity of acetaldehyde; w is the rate of its formation, and x is its concentration.

The amount of acetaldehyde formed at rate w in time t , its further oxidation not being taken into account, is

$$c = \frac{t}{\theta} w dt. \quad (5)$$

Substituting the value of w from Equations 4 and 5, we obtain

$$c = \frac{\alpha_0}{\alpha} x d \ln \alpha. \quad (6)$$

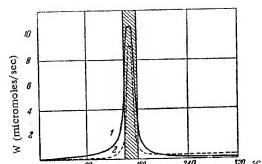


Fig. 6. Rates of formation (Curve 1) and consumption (Curve 2) of acetaldehyde in the cool-flame oxidation of propane

Having constructed the curve $x = f(\ln \alpha)$, we find c by graphical integration. The kinetics of the formation of acetaldehyde - its further oxidation not being taken into account - is shown in Fig. 5. In this figure we give also the analogous curve obtained by Polyak and Shtern [9] in work on the cool-flame oxidation of propane under identical conditions. A comparison of the courses of the curves shows that, when the cool-flame zone is passed, Polyak's results are almost identical with ours. As regards the period of induction, there are serious discrepancies. It is probable that substantial corrections must be made in the method of calculation used by these authors.

Knowing the actual kinetics of the accumulation of acetaldehyde, we may determine its rate of formation by graphical differentiation of the curve $c = f(t)$ (Fig. 5). The difference between the rates of formation and accumulation (the latter is found by graphical differentiation of Curve 1, Fig. 4) gives the rate of consumption. The rates so calculated are represented in Fig. 6, from which it will be seen that both formation and consumption occur throughout the whole course of the oxidation as far as the extinction of the cool flames. After the extinction of the cool flames the rate of formation of acetaldehyde falls almost to zero, although the rate of its consumption still remains appreciable.

Our conclusions are in conflict with those of Feklisov and Nelman [2] in their work on the behavior of acetaldehyde in the oxidation of butane.

Taking into account the fact that carbon dioxide is an end product of the oxidation and that carbon monoxide is not converted appreciably into dioxide, we calculated the rate of formation of these compounds from the carbonyl group of acetaldehyde and from other products. The rate of formation is found from the equation

$$w_1 = \frac{1}{\alpha_{\text{CH}_3\text{CHO}}} \frac{dI}{dt} \quad (7)$$

In which w_1 is the rate of formation of CO or CO_2 from acetaldehyde and $\frac{dI}{dt}$ is the rate of change of total activity of CO or CO_2 . The rate of formation of CO or CO_2 by other routes w_2 is the difference between the rate of accumulation w and the rate of formation from acetaldehyde:

$$w_2 = w - w_1 \quad (8)$$

These rates were calculated from data obtained by analysis of the products before the formation of and after the extinction of the cool flames.

The results of the calculation are given in the table.

TABLE I
Rates of Formation of CO and CO_2 from Acetaldehyde and other Oxidation Products

Duration of reaction (seconds)	Reaction product	Concentration (molecules / liter)	Specific activity (molecules / mmole) $\times 10^3$	Total activity (molecules / mmole) $\times 10^3$	Rate of formation from other products (molecule / second)	Rate of formation from other products (molecule / second)
140	CO	0.1006	2.31	2.3	0.0041	0.013
160	CO	0.0380	2.27	2.2	0.0041	0.013
140	CO_2	0.0394	15.7	6.2	0.008	0.009
160	CO_2	0.1270	7.9	7.9	0.008	0.009

The table shows that the rate of formation of CO from acetaldehyde in the cool-flame zone is only one-third of the rate of formation by other routes. Carbon dioxide is formed from acetaldehyde and from other products at approximately equal rates. It follows from these considerations that in the cool-flame zone about one-half of the CO_2 and about 30% of the CO are formed from the carbonyl group of the acetaldehyde.

SUMMARY

- It was shown by the blowing method that acetaldehyde can be determined polarographically in the products of the oxidation of propane.
- It was shown that at temperatures up to 39° no hydrogen transfer occurs in alcohol-acetaldehyde mixtures.
- It was shown that most of the carbon dioxide produced in the oxidation of propane is not formed by the oxidation of carbon monoxide.
- It was shown that in the oxidation of propane, acetaldehyde is formed and consumed at comparable rates.
- It was shown that in the cool-flame zone, about 50% of the carbon dioxide and 30% of the carbon monoxide are formed from the carbonyl group of acetaldehyde.

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* T.p. = C. B. Translation pagination.

CRITERIA FOR CHAIN REACTIONS

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The main features distinguishing chain and radical processes from molecular processes are considered to be certain kinetic peculiarities, marked critical phenomena (in branched chain reactions), anomalously high quantum yields (in photochemical chain processes), appreciable acceleration or retardation when small additions are made, fundamental changes in kinetics when free radicals are added to the reacting system, etc. [1]. It must be noted that these criteria enable us to make a choice between chain, radical, and molecular mechanisms only when the relevant experiments give positive results. If, however, one or more than one listed characteristics are absent, then it is generally not possible to affirm on this basis that a process is definitely a molecular one. It is often no less difficult to establish whether a reaction in which radicals take part is a chain reaction or simply a radical reaction.

An approach may be made to the solution of problems relating to the mechanism of a complex reaction on the basis of an analysis of the general problem of the concentrations of free radicals in the course of a chemical transformation. In fact, an examination of the usual chain reaction schemes, both for branched and for unbranched processes, leads to the conclusion that the high rates of such processes are associated with the formation, in the course of the reaction, of higher than equilibrium concentrations of free radicals (with respect to equilibrium with the original reactants). In purely radical thermal reactions, the concentrations of free radicals are always less than the equilibrium concentrations. On the other hand, in molecular reactions, in which the final products are formed without the participation of radicals, the concentrations of the latter always correspond to equilibrium with the original molecules.

It follows from these considerations that the most direct method of determining the character of a chemical process would be the exact measurement, in the given system, of the concentrations of those radicals which could result in the formation of the final products, and comparison of the values obtained with equilibrium values. Our experimental methods, however, permit us to measure absolute concentrations of radicals only in systems in which $[R]$ attains a value of at least some hundredths of a millimolar (for example, $[H]$ and $[OH]$ in rarefied flames of hydrogen and carbon monoxide [2]). When the value of $[R]$ is appreciably less than this, as in such processes as the oxidation of hydrocarbons and unbranched chain reactions of halogenation, polymerization, thermal decomposition, etc., the direct does not appear to be possible. The exact determination of this ratio is rendered difficult also by the fact that absolute values of $[R]_{\text{equil}}$ can be calculated only very approximately for radicals that are at all complex; thermodynamic functions for such radicals are unknown, and the experimental determination of $[R]_{\text{equil}}$ is in most cases practically impossible. In spite of these difficulties, a choice between chain, radical, and molecular mechanisms may sometimes be made for processes which can be carried out reversibly under the conditions in which we are interested.

At the basis of the proposed method for the identification of the mechanism lies a quite obvious postulate, namely, that in an equilibrium system, the concentration of free radicals has its equilibrium value with respect to any of the reacting substances. Let us examine two reaction systems. In system (1) the reaction



proceeds with given concentrations of the starting substances (A_1), (A_2), ... under given conditions. In system

(2), under the same external conditions, to the original substances at the initial concentrations (A_1), (A_2), etc. the final products are added in concentrations exactly corresponding to equilibrium conditions. It is quite obvious that no chemical reaction will be observed in system (2); for example, the concentration of A_1 will not change with time. However, since chemical equilibrium has a dynamic character, in such an equilibrium system two opposed processes - the consumption and formation of A_1 - will be constantly proceeding at equal rates.

Let us compare the concentrations of like radicals (or the total concentrations of radicals) in the two systems for different assumptions regarding the mechanism of the process. If it is a molecular reaction, then for any of the radicals:

$$[R_1]_1 = [R_1]_{II} \text{ and } (\sum_i [R_i]_1)_I = (\sum_i [R_i]_{II})_I$$

If it is a radical reaction, then at least for one of the radicals of the system,

$$[R_1]_1 < [R_1]_{II} \text{ and } (\sum_i [R_i]_1)_I < (\sum_i [R_i]_{II})_I$$

If it is a chain reaction, then at least for one radical, and sometimes for all,

$$[R_1]_1 > [R_1]_{II} \text{ and } (\sum_i [R_i]_1)_I > (\sum_i [R_i]_{II})_I$$

Hence, in order to establish the main features of the mechanism, there is no need to measure the absolute concentrations of free radicals. For this purpose it is quite sufficient to determine relative concentrations and as a standard for comparison it is most convenient to select concentrations observed when the process is carried out under equilibrium conditions.

For the determination of relative concentrations of radicals, spectrum, magnetic-resonance, and mass-spectrometric methods can be used. We consider that in this way the question of the mechanism of the process - understood in the sense already indicated - can be solved unequivocally (only for reversible processes, of course).

Another approach to the solution of the question under consideration can be made by chemical methods in particular, by the method of labeled atoms. Since the concentration of free radicals (in the case of chain and radical reactions) is unequivocally associated with the rate of the process, a comparison of the rate of reaction (1) in system I (w_I) with the rate of the transformation of the original reactants in the same direction in system II (w_{II}) should enable us to distinguish between the mechanisms in which we are interested. The greatest difficulty lies in the discovery of a method for the separate determination of the forward and reverse reactions in reversible processes. The only method available at present for the solution of this problem is the method of labeled atoms. If we label the molecules of one of the components of the original mixture (e.g. A_1), then by the rate at which A_1^* is consumed (or the rate at which B_1^* is formed) we may form an idea of the rate of the forward reaction in the equilibrium system II in a number of cases. We consider that this method may enable us to make a very clear distinction between chain reactions on the one hand and radical and molecular reactions on the other.

In the case of molecular processes the rate reaction depends, by definition, only on the concentrations of the original substances, and, since these concentrations are the same in both systems,

$$w_I = w_{II},$$

in which w_{II} is the rate of reaction in system II measured with the aid of labeled atoms.

If the reaction (1) proceeds by a chain mechanism, then the rate at which the substance A is consumed can be written

$$-\frac{d[A_1]}{dt} = k[R_1](A_1),$$

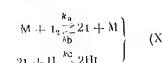
in which k is the rate constant for the elementary process of interaction between the molecule A and the corresponding radical of the system (in this case R_1). Since in the equilibrium system II $[R_1]$ is less than in

system I,

$$w_I > w_{II}.$$

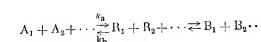
In radical mechanisms $[R_1]$ is greater than $[R_1]_I$, and it would be expected that w_{II} would be greater than w_I .

This relationship holds, however, only in radical processes in which the molecule containing the labeled atom does not dissociate into radicals. For example, if we assume that the iodination of hydrogen has the radical mechanism recently proposed by Semenov [3]:



and use deuterium or tritium as a labeled molecule, then it can be shown that the rate of consumption of H_2 under equilibrium conditions should be $(1 + k_2[H_2]/k_1[M])$ times as great as that obtained when reaction is carried out in absence of H_2 . Such experiments might enable us to make a choice between the scheme given above and a molecular mechanism.

However, in radical reactions in which the labeled molecule takes part in the formation of radicals, for example:



the rates w_I and w_{II} are found to be equal. This is explained by the fact that in such processes the values of w_I and w_{II} are not, strictly speaking, the rates of consumption of the original molecules, but are only differences between the rates of two reversible processes (a) and (b). Taking this circumstance into account, for radical reactions in general we find that

$$w_I \leq w_{II}.$$

The method of labeled atoms, therefore, is somewhat less versatile for the solution of our problem than any of the methods of determining relative concentrations of free radicals. It is, however, quite applicable as a criterion for chain mechanisms, which is a matter of great significance at the present time [3].

There are no data in the literature relating to the comparison of w_I and w_{II} in radical, chain, and molecular reactions. Similar considerations can be applied also in the analysis of data on the course of ionic and heterogeneous processes. In this connection we may mention the work of Wilson and Dickenson [4], in which data on the determination of w_{II} for the oxidation of arsenic acid labeled with radioactive arsenic to arsenic acid in presence of iodide ions were compared with the results of Roehl and others [5], who studied the same reaction under conditions far removed from equilibrium. As direct exchange between the two acids did not occur under the conditions of these experiments - as was shown by special experiments - the authors' suggestion that the process proceeds by a dissociation-association ionic mechanism appears very probable. The reaction scheme proposed by Roehl and others on the basis of kinetic data is based on the hypothesis that the determining stage is the reaction of the iodide ion (in the form I^-) with the undissociated arsenic acid molecule. Such a mechanism is quite analogous from the kinetic point of view to the radical mechanism discussed above. From our discussion it follows that in this case the rate of exchange in the equilibrium system (w_{II}) may be somewhat higher than the rate in a system in which the final product is absent (w_I). The numerical values of the effective constants given in the paper [4] are, respectively, 0.071 and 0.057 at 25° and 0.154 and 0.125 at 35° . It may therefore be considered that comparison of the values of w_I and w_{II} confirms the proposed mechanism.

SUMMARY

1. It is shown that molecular, chain, and radical reactions differ with respect to the concentrations of free radicals.
2. For the identification of chain reactions it is proposed that use should be made of the method of labeled atoms in order to compare the rates of the reaction $A \rightarrow B$ in absence of B and in presence of an equilibrium concentration of B.

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Institute of Chemical Physics of the
Academy of Sciences of the USSRPOSSIBILITY OF THE DETONATION OF
GAS MIXTURES IN CONICAL TUBES

S. M. Kogarko

In a previous paper we examined the possibility of initiating a spherical detonation wave in a space containing a gaseous mixture by means of an electric spark, an explosion, or the introduction of a shock wave. In the present paper we report the experimental results of a study of the detonation of gas mixtures in conical tubes and we make a theoretical examination of the conditions under which stable detonation is possible in a tube of constant section, in an infinite space, and in a conical tube.

Let us examine the conditions for the propagation of a stationary detonation wave in a tube of constant section.

It has been established experimentally that, in the propagation of a detonation wave in an explosive mixture contained in a tube of constant section, the wave velocity remains strictly constant over the whole length of the tube. In this case, the constancy of the velocity of the detonation wave is ensured by the constancy of the amplitude of the shock wave that is being propagated in the detonation wave front. On the basis of present-day concepts relating to the processes occurring in a detonation wave, the detonation of a gaseous explosive mixture can be described as follows. A powerful shock wave is propagated through the mixture at the detonation velocity, and this compresses the original mixture so that it attains a high pressure and is raised to a temperature of 1000–2000°. Behind the shock wave there moves a layer $\underline{1}$ of compressed mixture in which the period of induction for the self-ignition of the mixture begins and ends. The length of this layer of the mixture is $1 \sim \tau(D - U)$, in which D is the detonation velocity and U is the mass velocity of the gas behind the shock wave. Moving behind the layer of compressed mixture is the reaction zone, in which the explosive chemical reaction is taking place. In this zone the chemical energy of the mixture is evolved and the composition of the mixture changes from its original state at the beginning of the zone to that of the reaction products at the end of the zone. This complex system, consisting of the shock wave, the layer of compressed but not yet reacting mixture, and the reaction zone, moving as a single unit at a constant velocity is the "detonation wave".

In the layer of the mixture compressed by the shock wave, in which the mixture stays during the induction period of self-ignition, no appreciable amount of the chemical energy of the mixture is given up. The compression of the original mixture occurs at the expense of the energy of the shock wave. Owing to the stationary nature of the detonation process, at any given moment the energy being expended by the shock wave in compressing the original mixture must be exactly counterbalanced by the energy entering the shock wave from the reaction zone. We shall assume that the energy expended by the shock wave in compressing the original mixture is proportional to the volume of the compressed mixture. For the detonation of a mixture in a cylindrical tube of constant cross section we may write the volumes of the original mixture that are compressed during two equal periods of time τ , from $t - \tau$ to \underline{t} and from \underline{t} to $t + \tau$, in the following form:

$$V(t - \tau),_t = \tau^2 \Gamma \quad \text{and} \quad V_t(t + \tau) = \tau^2 \Gamma,$$

in which Γ is the distance traversed by the shock wave through the original mixture during the induction period τ , and \underline{t} is the radius of the tube.

Let us now write down the ratio of the volume of the original mixture compressed by the shock wave during time τ beginning from the point of time $t - \tau$ to the volume of the original mixture compressed by

the shock wave for the same time τ but beginning from the point of time t_1 . This ratio is the ratio of energies expended by the shock wave in the compression of the original mixture during two successive periods of time τ in the course of the whole process of detonation of the mixture; it will characterize the stability of the shock wave in the detonation process. Let us denote this ratio by H_1 ; for a tube of constant section it will be:

$$H_1 = \frac{V_{t_1}(-\tau), t}{V_{t_1}(t + \tau)} = \frac{\pi R^2 t}{\pi R^2 t'} = 1 \quad (1)$$

Hence, in the detonation of a gas mixture in a tube of constant section, the energy expended by the shock wave in compressing the original mixture for a period τ will be the same in any two such successive periods, i.e., constant, and therefore the amplitude of the shock wave will also remain constant during the whole detonation process, i.e., the propagation of the shock wave through the mixture will be a stationary process.

The loss of energy from the chemical reaction zone at the walls of the tube resulting from the thermal conductivity of the gas and the friction of the gas against the walls will remain constant during the detonation process and so cannot affect the stability of the detonation wave differently at different times during the detonation of a mixture in a tube of constant section. This loss results in some reduction in the detonation velocity. The experimentally measured detonation velocity is always a few percent below the value calculated from classical detonation theory. The extent of this loss depends on the length of the reaction zone in the detonation wave. This loss increases at the detonation limits, and it results in an appreciable reduction in the detonation velocity. However, before the difference between the theoretically calculated detonation velocity and the experimentally determined value becomes considerable and exceeds 10-15% of the detonation velocity, the limit is reached and the stationary propagation of detonation ceases [1, 2]. Here, we are particularly drawing attention to the fact that the detonation wave can undergo stationary propagation through the mixture when there are losses from the reaction zone corresponding to a reduction in detonation velocity by 10-15% of its theoretical value.

Propagation of a Spherical Detonation Wave

The propagation of a spherical detonation wave through a gaseous explosive mixture will differ fundamentally from the propagation of a detonation wave through a mixture confined in a tube of constant section. As the propagation of a spherical detonation wave proceeds, the surface of the shock wave will increase, and with increase in this surface, the period of induction for self-ignition of the mixture compressed by the spherical shock wave being constant, an increase will occur also in the volume of the original mixture that will be compressed by the spherical shock wave in the period τ . In any given short interval of time the spherical shock wave will always compress a greater amount of the original mixture than in the immediately preceding equal interval, but the spherical shock wave will be supported from the reaction zone by the chemical energy of a mixture compressed in a preceding interval of time; it follows that, in the propagation of a spherical detonation wave, there will always be some weakening of the shock wave. The weakening of the spherical shock wave arises from the lack of equality between the amounts of energy expended by the shock wave on the compression of the original mixture in two successive short intervals of time.

Let us examine what will happen with a spherical shock wave when the mixture is detonated in the center of a large space. At time t_1 let the radius of a shock wave characterized by the same parameters as a plane shock wave formed by detonation of the same mixture in a tube of constant section have the value $r + 1/2 l'$, in which l' is the length of the layer of original mixture compressed by the spherical shock wave during a time corresponding to the induction period τ for self-ignition of the mixture at the temperature and pressure corresponding to the given shock wave, and r is the average radius of the spherical shock wave for the interval of time from $t - \tau$ to t_1 . The volume of the original mixture compressed by the spherical shock wave in the interval of time from $t - \tau$ to t_1 will be determined by the following equation:

$$V_{(t-\tau), t} = 4\pi r^2 l'$$

The volume of the original mixture compressed by the spherical shock wave in the interval of time from t to $t + \tau$ will be determined by the following equation:

$$V_{t, (t+\tau)} = 4\pi (t + \tau)^2 l'$$

Assuming, as we did previously, that the energy expended by the shock wave in compressing the original mixture is proportional to the amount of mixture compressed, we may evaluate indirectly the change in the amplitude of the spherical shock wave from one interval of time to the next from the amount of energy expended by the shock wave in the compression of the original mixture in these two successive intervals of time. Let us write down the ratio of the volumes of the original mixture compressed by the spherical shock wave in the two successive intervals of time $t - \tau$ to t and to $t + \tau$. This ratio will correspond to the ratio of the energies expended by the shock wave in compressing the original mixture for these two successive intervals of time. Denoting this ratio by H_2 , we obtain:

$$H_2 = \frac{4\pi r^2 l'}{4\pi (t + \tau)^2 l'} = \frac{r^2}{(t + \tau)^2} = \frac{1}{1 + 2 \frac{t}{r} + \left(\frac{t}{r}\right)^2} \quad (2)$$

For all positive values of t and r this ratio will be less than unity. It follows quite obviously that a spherical shock wave will always expend more energy in one interval of time than in the preceding interval. Another more important conclusion that can be drawn from an analysis of this expression is that the enfeeblement of a spherical shock wave in a mixture of constant period of induction for self-ignition will become less as the radius of the shock wave increases. A third conclusion is that, in different gaseous explosive mixtures having different periods of induction, the spherical shock wave will be enfeebled to the same extent in each mixture not when the radii of the shock waves are the same, but for a constant value of l'/r , which is proportional to the ratio that the induction period for self-ignition of the mixture compressed by the spherical shock wave bears to the radius of the shock wave, since $l' = rD$ (D is the detonation velocity). Hence, when the enfeeblement of the spherical shock wave is still within the permissible limit, within which the breakdown of the spherical detonation wave does not yet occur, the initiation of spherical detonation waves in different gaseous explosive mixtures will be effected by spherical shock waves that will differ both in amplitude and extent.

Every gaseous explosive mixture will be characterized by a minimum critical spherical shock wave capable of initiating the spherical detonation of the mixture. In Fig. 1 the relationship between H_2 , calculated from Equation 2, and $\log l'/r$ is shown graphically.

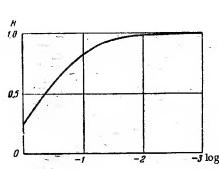


Fig. 1. Dependence of the spherical shock wave on l'/r .

The enfeeblement of the spherical shock wave in the spherical detonation of a gaseous explosive mixture depends not only on the value of the period of induction for self-ignition τ , expressed as the length of the layer of original gas compressed by the shock wave but not yet undergoing reaction, but also on the ratio of the period

of induction to the radius of the spherical shock wave. Hence, in a gaseous explosive mixture for which the period of induction for self-ignition of the mixture compressed by the shock wave is τ and for which detonation is possible in a tube of constant section, it is possible to create a spherical shock wave of radius r such that the ratio l/r will have less than the critical value. Hence, in a gaseous explosive mixture that is capable of detonation in a tube of constant section, spherical detonation can be initiated under certain experimental conditions.

Propagation of a Detonation Wave in a Conical Tube

From the considerations given above we concluded that, in the propagation of a detonation wave through a mixture in a tube of constant section, the shock wave always compresses the same amount of the original mixture in a given short interval of time τ throughout the whole detonation process. At any given time in the course of the process, the energy expended by the shock wave in compressing the original mixture is precisely counterbalanced by the energy entering the shock wave from the chemical-reaction zone of the detonation wave. What will happen with the shock wave that is propagated in the detonation wave front if we allow the detonation wave, which is undergoing stationary propagation through a mixture in a tube of constant section, to pass into a tube of variable section, i.e., a cone, filled with the same mixture?

Let us write down the ratio of the volume of the original mixture compressed by the shock wave in the time τ required for the detonation wave to move a distance l along a tube of constant section to the volume of the original mixture compressed by the shock wave in the same interval of time τ when the detonation wave moves a distance l in the cone. The volume of the original mixture compressed by the shock wave in time τ in the tube of constant section is $V_k = \pi r^2 l$. The volume of the original mixture compressed by the shock wave in time τ in the cone is $V_v = \frac{1}{3} \pi r^2 l (\frac{r}{a} + ar + \frac{1}{3} a^2)$.

$$V_v = \frac{1}{3} \pi r^2 l (\frac{r}{a} + ar + \frac{1}{3} a^2) = \pi r^2 l \left(r^2 + ar + \frac{1}{3} a^2 \right),$$

where

$$a = l \tan \frac{1}{2} \alpha$$

α being the angle of the cone.

The ratio of the volumes is given by

$$H = \frac{V_v}{V_k} = \frac{\pi r^2 l (\frac{r}{a} + ar + \frac{1}{3} a^2)}{\pi r^2 l} = \frac{1}{1 + \frac{a}{r} + \frac{1}{3} \left(\frac{a}{r} \right)^2} \quad (3)$$

For all positive values of a and α , the value of this ratio will always be less than unity. Hence, when the detonation wave passes from a tube of constant section into a cone, the shock wave will be weakened. However, the extent to which it will be weakened may be made as small as we like by suitable choice of the values of a and α . The angle of the cone determines the extent to which the surface of the shock wave increases per unit length, i.e., the extent to which the shock wave is weakened. For every gaseous explosive mixture that is capable of undergoing detonation there is a permissible weakening of the shock wave such that further weakening makes stationary detonation of the mixture impossible; hence, the dimensions of the cone leading from a smaller to a larger tube are immaterial for the determination of whether a detonation wave will pass from one tube to the other without being broken down.

Experimental Investigation of the Propagation of a Detonation Wave in a Conical Tube

For the investigation of the permissible weakening of the detonation wave the conical tube method was used. In this method, by varying the diameter of the entry tube and the angle of the cone we may vary the extent to which the wave is weakened within wide limits.

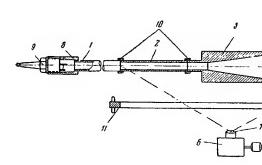


Fig. 2. Diagram of experimental arrangement

A diagram of the apparatus is given in Fig. 2. It consisted of a metal tube 1, 1200 mm in length, a glass tube 2 of the same internal diameter as the metal tube, a metal cone 3, a wide glass tube 4, one end of which was closed by the rubber stopper 5, a recording camera 6 with its objective 7, and connecting tubes for removing reaction products from the apparatus and for filling it with the gaseous explosive mixture under investigation. One end of the metal tube 1 was soldered into the cap 8, which contained the spark plug 9. The metal tube 1 at its open end, the glass tube 2, the metal cone 3, and the wide glass tube 4 were all firmly fixed together at their end surfaces with the aid of short pieces of rubber tubing 10. The part of the apparatus that was filled with the explosive mixture and was shattered in the experiment was separated from the camera by the shield 11, in which a 10-mm slit was made to permit the photorecording of the propagation of flame in the glass part of the apparatus. The ignition of the mixture was carried out in the metal cap, either by burning a fine copper wire fixed to the electrodes of the spark plug, or, in mixtures highly diluted with nitrogen, by exploding a small amount of lead azide.

The following results were obtained. In the mixture $2\text{H}_2 + \text{O}_2$, the detonation wave progressed along a tube of internal diameter 5 mm and passed without being broken down through a 5 mm/35 mm cone of angle $\alpha = 11^\circ 30'$ into a tube of internal diameter 35 mm. When the angle of the cone was increased to $23^\circ 0'$, the detonation wave broke down in a 5 mm/35 mm cone. When the diameter of the first cylindrical tube was increased from 5 to 8 mm, the detonation wave in the $2\text{H}_2 + \text{O}_2$ mixture passed an 8 mm/38 mm cone of angle $\alpha = 23^\circ 0'$ without breaking down, but was broken down in an 8 mm/38 mm cone of angle $\alpha = 33^\circ 30'$.

Two photorecordings of the propagation of flame fronts through glass tubes placed before and after a cone are shown in Figures 3A and 3B. The photorecordings correspond to the movement of the flame front from top to bottom and the movement of the film from left to right. The upper white band corresponds to the propagation of the flame front and the incandescence of the reaction products in the narrow glass tube placed before the cone, and the lower white band corresponds to the propagation of the flame front and the incandescence of the reaction products in the wide glass tube placed after the cone. The black band sandwiched between the white bands corresponds to the length of the metal cone, in which the flame front is not photographed.

Photorecording 3A corresponds to the propagation of a detonation wave through the mixture $2\text{H}_2 + \text{O}_2$ in a glass tube of internal diameter 8 mm, followed by an 8 mm/38 mm metal cone of angle $\alpha = 23^\circ 0'$ and a glass tube of internal diameter 38 mm. As can be seen from the photorecording, the detonation wave front is propagated with the same strictly constant velocity both in the 8-mm glass tube and also in the 38-mm glass tube that follows the cone. Detonation velocity in glass tubes was 2790 m per second; average value in cone was 2660 m/sec. Detonation wave propagation rate is reduced in the cone, but the wave is not broken down. Photorecord-

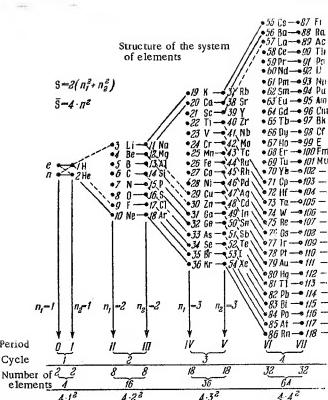


Fig. 1. Stepwise form of the Mendeleev periodic system of the chemical elements.

It follows that for atoms which for some cause or other have lost their correct electronic envelope, the Mendeleev periodic law will not be applicable.

Although this assertion can be regarded as indisputable, if it is not subjected to special examination and investigation it nevertheless remains as nothing more than a mere declaration. It is not difficult to establish the direction that a theoretical investigation must take; it arises quite naturally in the study of the atomic envelopes from the point of view of the Pauli exclusion principle. As is well known, the source of individuality that is so characteristic of the Mendeleev system is expressed by this principle, which asserts the impossibility for any two electrons in the same atom to have their four quantum numbers identical.

It is well known also, however, that the Pauli principle is not sufficient for the derivation of the periodic law and system. It is necessary to have recourse to the concept of uncompleted electron shells in atoms, as an example of which we may take calcium, for which it is found that it is energetically more favorable for the two outer electrons to go into the fourth energy level, in spite of the possibility in principle for them to go into the third level, which is not yet completed (Table 1).

It appears to be quite possible to transfer these two electrons by external action into the lower orbital 3d. In order to do this it is necessary to apply pressure sufficient to compress the electron envelopes. The electrons will then pass to an orbital that is closer to the nucleus without in any way acting contrary to the Pauli principle. Here an important and interesting question arises: will this treatment alter the chemical nature of calcium as an element? Undoubtedly yes, for its electronic structure will become quite different, as will be seen clearly from Table 2.

Table 1						
1 s	2 s	2 p	3 s	3 p	3 d	4 s
Ca ²⁺	2	2	6	2	6	—
K ⁺	2	2	6	2	6	2
Table 2						
1 s	2 s	2 p	3 s	3 p	3 d	4 s
Ca ²⁺	2	2	6	2	6	2
Ti ⁺	2	2	6	2	6	—

Table 3						
1 s	2 s	2 p	3 s	3 p	3 d	4 s
K ⁺	2	2	6	2	6	2
Fe ²⁺	2	2	6	2	6	—
Fe ³⁺	2	2	6	2	6	8
Ni ²⁺	2	2	6	2	6	—

After the above-described transformation of the atom, its nucleus will remain unaffected - a fact, however, that is irrelevant, since the nucleus takes no part in chemical processes. The number of electrons also remains unchanged. The chemical characteristics will change, however, because both the electron orbitals and the energy of the electrons have changed. For the same electronic "composition", the arrangement of the electrons in space has become different - we meet the phenomenon of electronic isomerism of atoms. We shall refer to the isomer of the calcium atom as "bocalcium" and denote it by Ca²⁺; it already has different, what might be called degenerate, chemical properties. This difference in properties arises from a difference in structure: the localization of the outer electrons in the fourth shell previously resulted in the appearance of the element in the fourth period of the system, whereas the electrons do not now extend beyond the third shell, so that the element must appear in the third period of the system, "bocalcium" may now be regarded more as an analog of a known titanium ion, as can be seen from Table 2.

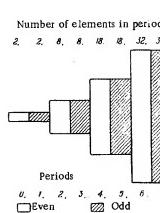


Fig. 2. Diagrammatic representation of the alternation of even and odd periods in the Mendeleev system.

ods and its atoms with incomplete inner shells is divided into seven periods (Fig. 2), the new system of "degener-

The iron atom provides another curious example of atomic isomerism. In Table 3 we present the normal iron atom, its electronic isomer "isoiron", and its "partial" isomer (only electronic isomerism is present, the nuclear charges being different) or analog of "isoiron" - the ordinary nickel ion.

The electronic isomerization of atoms under pressure is therefore able to alter their chemical properties substantially, for their chemistry is determined by the electronic structure of the outer shells; this is what we have called the degeneration of the chemical properties of the atoms. This peculiar forcing of the electrons into lower, incomplete shells without violation of the exclusion principle - which is possible for elements standing after neon, i.e., beginning from the third period - has, of course, a radical effect both on the properties of the element and, therefore, on its position in the periodic system.

Whereas the well known form of the Mendeleev system with its alternating pairs of even and odd per-

etc. atoms must have a much simpler appearance and will contain only five periods instead of seven. At what pressures can such transformations of atoms be brought about? With the aid of the quantum theory of metals developed by Wigner and Seitz Sternheimer [5] calculated the work required for the transfer of an electron from the 6f to the 5d level in the cesium atom. We recalculated his results in terms of pressure and obtained a value of 45,000 atm. Such a pressure is quite realizable, even under laboratory conditions. It is true that for cesium, which has a high atomic radius, this work has its least value; for other atoms it may be 2-3 times as great. Nevertheless, this and other investigations show that for pressures of the order of 50,000-120,000 atm upwards electronic isomerization is quite possible.

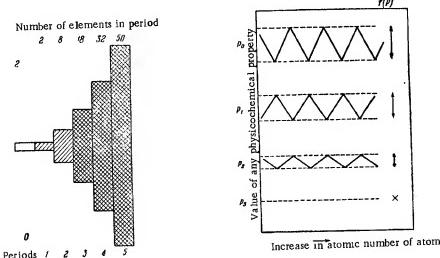


Fig. 3. Diagram of a periodic system containing atoms having degenerate chemical properties (cross-shading).

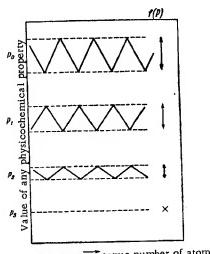
The periodic system of chemical elements corresponds to these thermodynamic conditions is still completely consistent with the Pauli principle. The atoms do not contain "vacant" or incomplete quantum levels. The boundaries of these periods (not counting the zero period) will, as before, lie at helium and neon in the first and second periods, which will preserve their normal structures, and then - in the periods corresponding to elements having "degenerate" chemical properties - they will lie at nickel in the third period and at neodymium in the fourth (Fig. 3).

We shall now try to make an approach to the question of the realizability of still deeper transformations in atomic structure, resulting no longer in changes in the chemistry of the elements, but in the complete disappearance of chemistry.

A rigorous solution of the question is again impossible, and existing data enable us to make only very crude approximations in our approach. Even here, however, this approach can be checked - by quantum-mechanical calculations (for example, Ramsey's calculations for hydrogen) and, as we shall see below, by comparison with seismometric data. As usual in geochemistry, we shall use graphs in which pressures are represented on a logarithmic scale, which is always convenient when operating with high numbers; for us, the essential matter is only the obtaining of a more or less smooth curve passing through all points and the plotting of the corresponding seismological data on the same graph - the equation of the curve is immaterial.

In order to answer this question it is necessary to examine the relationship between the periodic changes of various properties and pressure. Unfortunately, our choice of properties is at present extremely limited: there is adequate information on only one property, namely, compressibility.

Fig. 4. Diagram of "periodicity function" $f(p)$ at various pressures. The values of the "periodicity function" at various pressures are represented by the arrows at the right of the diagram.



Richards established periodicity in the relationship between the compressibility of the elements and atomic weight. On the basis of Bridgman's data for 30,000 and 100,000 atm, Vereshchagin and Likhitev [6] showed that this periodicity persists up to these high pressures, although it becomes progressively less distinct. This can be best seen from Fig. 4, in which from top to bottom - from low pressures to high - the reduction in the range of the periodicity in the relationship between this property and atomic number is represented in crude diagrammatic fashion. Let us introduce the periodicity function $f(p)$, this being the distance (the arrow on the right in Fig. 4) between the broken lines marking the limits of the variations observed: it may be said to give the "sweep" of the periodic variations. It is clear that the lower the value of this function, the less marked is the periodicity, and its attainment of the value zero corresponds to the complete disappearance of periodicity.

TABLE 4

Pressure p (atm)	Periodicity function $f(p)$	Logarithm of pressure ($\log p$)	Depth h (km)
1	2.5	0.00	-
30,000	1.3	4.48	-
100,000	0.9	5.00	-
(1,400,000)	0.0	(6.15)	(2,900)

Table 4 gives the periodicity function, which we have calculated from Vereshchagin and Likhitev's data, in its dependence on pressure, expressed, as already stated, as $\log p$ (Fig. 5). We give also the depth below the earth's surface corresponding to a given pressure. Although it is highly probable that a somewhat different picture will be obtained for some property other than compressibility, there is no reason to suppose that the difference will be very great, and the data that we already have may therefore be used in the formulation of certain generalizations.

Fig. 5. Graph of the change of the periodicity function with pressure.

In Fig. 5 points representing the tabular data lie on a smooth curve, which passes through a point for which the periodicity function has zero value at a pressure of approximately 1,400,000 atm ($\log p = 6.15$). Although this is a very rough extrapolation, in which there may be an error of as much as 100,000 atm, the value will be of the right order. At such pressures, therefore, all chemical properties of matter disappear, the regular layered arrangement of electrons around the atomic nucleus disappears, and we are left merely with "impersonal" nuclei immersed in a general electronic plasma - a universal metallic state of matter.

Can we find any experimental support - if not direct, then at least indirect - of the correctness, with respect to order of magnitude, of our estimates of the quantities under consideration? An answer is found in seismological data.

A study of the passage of seismic waves [7] in different directions through the earth indicates definitely the existence of two important thresholds in the state of matter: a rather diffuse one at a depth of about 100 km corresponding to the thickness of the earth's crust (the so-called Mohorovitch surface), and another at a depth of 2900 km. The pressure at the first depth ranges from 50,000-100,000 atm, and at the second it is about 1,400,000 atm, in close accord with the estimates that we made by a method quite independent of geophysical and geochemical methods. Inasmuch as homogeneity of phase (more accurately, aggregate invariability) throughout the whole depth of the earth is no longer a matter of doubt, it is difficult to regard this agreement

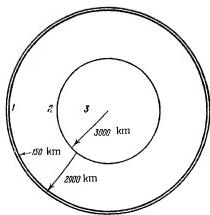


Fig. 6. Zones of the earth: 1) zone of normal chemistry; 2) zone of degenerate chemistry; 3) zone of zero chemistry

geologic geosphere, and core having boundaries characterized by the same pressures and depths; it therefore complements the geological picture from the viewpoint of chemistry.

Such, therefore, are the effects of high and superhigh pressures on the properties of atoms. In this way, from purely theoretical considerations, we can predict the electronic ionization of atoms with consequent radical changes in their chemical properties and therefore in the whole structure of Mendeleev's periodic system of elements; and we can predict also the complete annihilation of chemistry, corresponding to complete breakdown in the functioning of the Mendeleev periodic law for the atoms of the elements. These considerations, taken in conjunction with a consideration of the increase in pressure with increase of depth below the earth's surface, enables us to divide the earth into three geospheres - the geospheres of normal, degenerate, and zero chemistry.

This is not all, however; for without confining ourselves to the qualitative side of the solution of the problem, we can not envisage a quantitative approach that will render our solution more precise. Our extremely tentative estimates of the effect of pressure on the structure of electron envelopes correspond in order of magnitude with seismological and geological estimates of the pressures characteristic of the boundaries of these depth zones of our planet - the boundaries of the crust and of the core or centrisphere. In this way we can envisage the possibility of a more or less quantitative estimate of the probable limits of applicability of the Mendeleev periodic law of the elements in nature.

Like every other rigorous and rational limitation of the applicability of a scientific generalization, this one can only consolidate and further confirm this extremely important law of chemistry.

SUMMARY

As the atoms of the elements are compressed under pressures rising to superhigh values, a) at first electrons pass into unfilled levels permitted by the Pauli exclusion principle, with the result that "degeneration" of the normal chemical properties of the atoms occurs and the whole structure of the periodic system of elements changes its form; and b) the "crushing" of the electronic envelope then occurs with delocalization of electrons, complete loss of the chemical distinctions between the particles, and formation of a universal metallic state of matter.

The paper examines the thermodynamics, quantum-chemical, and seismological data that support the above-stated views, and a hypothesis is advanced concerning the zonal structure of the interior of the earth and the physicochemical properties of the geochemical shells.

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* T.p. = C. B. Translation pagination.

nitriles was not accompanied by the formation of ketones or the entry of phenyl into the benzene ring. The formation of nitrile trimers, which arise during the decomposition of benzenediazonium fluoroborate in nitriles probably as a result of the polymerizing action of boron trifluoride, was not observed in the decomposition of benzenediazonium fluorosilicate in nitriles.

The products of the decomposition of benzenediazonium fluorosilicate in acetophenone were the same as those obtained from benzenediazonium fluoroborate in the same medium and were different from the products of the decomposition of homolytically decomposing diazo compounds in acetophenone. During the decomposition of benzenediazonium fluorosilicate in acetophenone, the phenyl cation entered the benzene ring of the acetophenone. The phenyl cation entered mainly the position meta to the acetyl group, as was shown by the conversion of the corresponding fraction into 3-biphenylcarboxylic acid by the haloform reaction. To a less extent phenyl entered also the para position, and 4'-phenylacetophenone was isolated. The meta and para isomers were obtained in the proportions of 4 : 1. It is again necessary to take the comparative feebleness of the meta-orienting power of the acetyl group into account. In the decomposition of the homolytically decomposing diazo compound potassium phenylazideformate in acetophenone [7] phenyl did not enter the benzene ring, the reaction product being the dimer of the $\text{C}_6\text{H}_5\text{COCH}_3$ radical, 1,4-diphenyl-1,4-butanedione.

Thus, phenyl formed in the decomposition of benzenediazonium fluorosilicate attacks the nitrile molecule at the point of highest electron density - the nitrogen of the nitrile group - and the meta position in a benzene ring containing a meta-orienting substituent (the alkoxyacarbonyl group of a benzoic ester), which indicates the cationoid character of this phenyl and the heterolytic type of decomposition of the diazonium salt that generates it.

EXPERIMENTAL

Decomposition of Benzenediazonium Fluosilicate

The reaction was carried out in a four-necked flask fitted with oil-sealed stirrer, reflux condenser, and thermometer. The fourth neck served for the introduction of the diazonium salt.

a) Decomposition of Nitrobenzene. Over a period of two hours 40 g of benzenediazonium fluosilicate was added in small portions to 150 g of nitrobenzene at 75°. The reaction mixture became dark-colored, the temperature rose slightly, and faint fumes were observed. When the addition of fluosilicate was complete, the temperature was raised to 80° and the reaction mixture frothed slightly for a short time. The mixture was stirred at 80–80° for 45 minutes. On the next day benzene was poured onto the thick dark-colored reaction mixture and a tar separated, which was washed many times with benzene. The benzene extracts were washed with 10% caustic soda (some resin separated and was filtered off) and with water. They were dried over sodium sulfate, and benzene and nitrobenzene were distilled off, the latter under reduced pressure. Distillation of the residue gave 2.5 g of product, m.p. 150–164 (7 mm). This substance crystallized out completely and, after crystallization from methanol, its melting point and the melting point of a mixture with known 3-nitrobenzylphenyl were 60°.

b) Decomposition in Methyl Benzoate. The diazonium salt (33 g) was added over a period of 45 minutes to 116 g of methyl benzoate at 105°. Decomposition began immediately with evolution of white fumes. When addition was complete, the mixture was maintained at 150° for one hour. On the next day the reaction mixture was dissolved in ether, and the ether solution was washed with 10% caustic soda and then water. The solution was dried over sodium sulfate, ether was distilled off, and the residue was vacuum-distilled. The following fractions were obtained: Fraction I, b.p. up to 90° (4 mm) (methyl benzoate); Fraction II, 2.48 g, b.p. 125–150°, a liquid; Fraction III, 0.9 g, b.p. 150–165°, which partially crystallized out. Fraction II was hydrolyzed at the boil with 20 ml of 50% aqueous caustic soda for ten hours, some drops of unopened oil were extracted with ether, the alkaline layer was acidified with 15% sulfuric acid, excess of concentrated sodium carbonate solution was added, and the mixture was steam-distilled. The distillate gave a feeble reaction for phenol with ferric chloride and bromine water. The alkaline solution was acidified with sulfuric acid, and the precipitate that formed was crystallized from ethanol. The yield was 0.8 g, and the melting points of the product and of a mixture of the product with known 3-biphenylcarboxylic acid were identical (164°).

The precipitate that formed in Fraction III was crystallized from ethanol, and it then melted, both alone

and in mixture with known methyl 4-biphenylcarboxylate, at 117°. The filtrate from Fraction III was hydrolyzed and further treated under the conditions used for Fraction II. A feeble reaction was obtained for phenol in the distillate obtained from the sodium carbonate solution. The residue in the distillation flask was diluted with water, and the undissolved residue was filtered off and boiled with concentrated hydrochloric acid for 15–20 minutes. The precipitate formed was recrystallized from ethanol and then amounted to 0.05 g. Its melting point and the melting point of a mixture of the product with known 4-biphenylcarboxylic acid were identical (222°).

c) Decomposition in Ethyl Benzoate. The diazonium salt (38 g) was added over a period of 40 minutes to 130 g of ethyl benzoate at 105°. Bubbles of gas and white fumes were evolved. When addition was complete, the mixture was stirred at 110° for one hour. It was then dissolved in ether, and the ether solution was washed with 10% caustic soda and with water. The solution was dried with calcium chloride, and the ether and most of the ethyl benzoate were distilled off, the latter under reduced pressure. Vacuum distillation of the residue gave: Fraction I, b.p. 68° (3 mm) (ethyl benzoate); Fraction II, 1.1 g, b.p. 100–136° (3 mm); Fraction III, 3.8 g, b.p. 136–155° (3 mm). Fraction II, after hydrolysis and further treatment under the conditions used for Fraction II in the methyl benzoate experiment, gave a feeble reaction for phenol; the precipitate formed on acidification was found to be benzoic acid. When cooled, Fraction III partially crystallized. The crystals were separated and recrystallized from alcohol, when they amounted to 0.6 g, melting, both alone and in admixture with known phenyl benzoate, at 69–70°.

The oil separated from the crystals was hydrolyzed at the boil with 30% methanolic caustic soda. Methanol was then distilled off, water was added, and the undissolved residue was filtered off, boiled with concentrated hydrochloric acid, and recrystallized from ethanol (yield 0.08 g). Its melting point, alone and in admixture with known 4-biphenylcarboxylic acid, was 222°. The filtrate from the precipitate of sodium 4-biphenylcarboxylate was acidified, and the precipitate formed was recrystallized from petroleum ether and ethanol (yield 1.01 g). Its melting point, alone and in admixture with known 3-biphenylcarboxylic acid, was 163–164°.

d) Decomposition in Benzonitrile. The diazonium salt (38 g) was added over a period of one hour to 74 g of benzonitrile at 90°. The mixture was then maintained at 80° for one hour. The mixture was dissolved in ether, and the solution was washed with 10% caustic soda, when a precipitate formed and was filtered off (Precipitate A). The ether solution was washed with water and dried with calcium chloride. Ether was distilled off, and benzonitrile was distilled off under reduced pressure. Vacuum distillation of the residue yielded: Fraction I, 2.5 g, b.p. 73–100° (3 mm); Fraction II, 7.4 g, b.p. 166–200° (3 mm); Fraction III, 3.02 g, b.p. 255–275° (3 mm).

Fraction I partially crystallized. The crystals were separated from the oil and recrystallized from alcohol (1.3 g, m.p. 163°). Fraction II crystallized completely; after recrystallization from alcohol its melting point, alone and admixture with known benzonitrile, was 163°. Fraction III was a caramel-like viscous mass, from which by crystallization and freezing we succeeded in isolating a further 3 g of benzonitrile. Precipitate A (1.5 g, m.p. 163°) was also found to be benzonitrile. The total yield of benzonitrile was 10.95 g (28%).

e) Decomposition in Phenylacetoneitrile. Benzenediazonium fluosilicate (42 g, i.e. 1 mole) was added over a period of 90 minutes to 70 g (5 moles) of phenylacetoneitrile at 90°. The reaction mixture immediately became dark-colored, and decomposition proceeded vigorously with evolution of white fumes and nitrogen. The mixture was maintained at 80° for one hour. The mixture was cooled and dissolved in ether. The ether solution was washed with 10% caustic soda solution and with water, and it was then dried over sodium sulfate. Ether and phenylacetoneitrile were distilled off, and vacuum distillation of the residue gave: Fraction I, 6 g, b.p. 155–195° (5 mm), and Fraction II, 14.7 g, b.p. 200–240° (5 mm).

Fraction I partially crystallized. The crystals were filtered off and recrystallized from heptane and ethanol (yield 4 g). The melting point of the product, alone and in admixture with known 2-phenylacetanilide, was 114°. Fraction II crystallized completely and melted at 114° after recrystallization from alcohol. The total yield of 2-phenylacetanilide was 18.7 g (36%). Solvent was distilled from the mother liquors from the crystallization of 2-phenylacetanilide, and they were then boiled with concentrated hydrochloric acid for 12 hours. The hydrochloric acid solution was steam-distilled. The distillate was extracted with ether. The ether was distilled off, and the residue was made alkaline and again steam-distilled; the second distillate

was extracted with ether. The extract was dried and ether was distilled off, when a few drops of a viscous oil remained. Treatment of this with 2,4-dinitrophenylhydrazine in ethanol and hydrochloric acid gave a very small amount of a precipitate melting at 231-234° (the 2,4-dinitrophenylhydrazone of deoxybenzoin melts at 204°).

Decomposition in Acetophenone. Benzenediazonium fluorosilicate (42 g, i.e., 1 mole) was added over a period of 90 minutes to 71.6 g (5 moles) of acetophenone at 75°. During the addition the temperature rose to 80°, and it was maintained at 80° for one hour. The mixture was cooled and dissolved in ether. The ether solution was washed with 10% caustic soda and with water, and it was then dried with sodium sulfate. Ether was distilled off, and most of the acetophenone was distilled off under reduced pressure. Vacuum distillation of the residue gave: Fraction I, 3.5 g, b.p. 125-120° (5 mm); Fraction II, 5.6 g, b.p. 120-205° (5 mm); Fraction III, 6.3 g, 205-265° (5 mm).

Fraction II was again vacuum-fractionated: Fraction I', 0.31 g, b.p. 100-150° (5 mm); Fraction II', 1.63 g, b.p. 157-159° (5 mm); Fraction III', 1.26 g, b.p. 159-160° (5 mm).

A solution of Fraction II' in dioxane was treated with a solution of iodine in alkaline potassium iodide solution. The iodoketone formed was filtered off, and dioxane was distilled from the filtrate. When the product was acidified with hydrochloric acid, a precipitate formed and was crystallized from ethanol, when it melted at 162-163°, both alone and when mixed with known 3-biphenylcarboxylic acid. Fraction III solidified and was crystallized from acetone (yield 0.4 g); its melting point, both alone and in admixture with known 4'-phenylacetophenone, was then 118-119°. Fraction III was subjected to the same haloform scission as Fraction IV'. The product was 1.8 g of 3-biphenylcarboxylic acid; after being crystallized from alcohol, it melted, both alone and in admixture with known 3-biphenylcarboxylic acid, at 162-163°. In all, 1.8 g of 3-biphenylcarboxylic acid was obtained.

SUMMARY

1. The phenyl that is formed when benzenediazonium fluorosilicate is decomposed in a medium consisting of a benzene derivative containing a meta-orienting group enters the latter in the meta position: in nitrobenzene it gives 3-nitrophenyl, in benzoic ester it gives mainly 3-biphenylcarboxylic acid (and also phenyl benzoate); in acetophenone it gives mainly 3'-phenylacetophenone. In benzonitrile and in phenylacetone type, the decomposition results in the formation of benzonitrile and 2-phenylacetanilide respectively.

2. These reactions prove that the decomposition of benzenediazonium fluorosilicate is of the heterolytic type, a phenol cation being formed.

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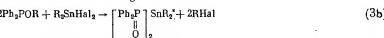
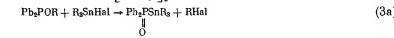
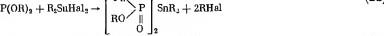
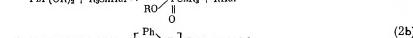
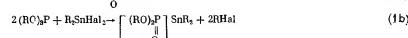
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Institute of Heteroorganic Compounds of the
Academy of Sciences of the USSR

* T.P. = C. B. Translation pagination.

STRUCTURE OF SOME ORGANIC COMPOUNDS CONTAINING TIN AND PHOSPHORUS

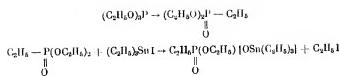
B. A. Arbuzov and N. P. Grechkin

Some years ago, in collaboration with Pudovik we prepared various types of organic compounds containing tin and phosphorus by the action of some alkyltin halides on esters of acids containing tervalent phosphorus [1-4]. Analogous syntheses were carried out by Arbuzov and Pudovik with alkylsilicon halides [5] and by Kamal and Belorosova with alkylarene halides [6]. We supposed that the course of these reactions would be analogous to that of the Arbuzov rearrangement, so that the products would contain direct linkages between tin and phosphorus and between silicon and phosphorus.



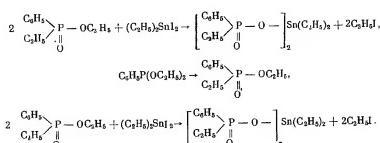
In the decomposition of such products with hydrochloric acid, it was to be expected that alkyltin chlorides would be formed together with phosphorus, phenylphosphorus, diphenylphosphorous acid, respectively. Actually, in all cases we succeeded in isolating the corresponding tin derivatives, but only in the decomposition of the products of reaction (3) did we isolate and identify diphenylphosphinic acid, the formation of which could be explained by the oxidation of the diphenylphosphinous acid originally formed.

In 1950 two papers by Malatesta and coworkers [7, 8] were published, and these express a different view on the course of the reactions (1), (2), (3), and (4) and the structure of the final tin-phosphorus and silicon-phosphorus organic compounds. Malatesta considers that in the reactions of triethyl phosphate with triethyltin iodide and with diethyltin diiodide, and also with bromotriethylsilane, the phosphorous ester is first isomerized into diethyl ethylphosphonite, which then, reacting with the halogen compound of tin or silicon, gives the corresponding mixed triethylstannyl or triethylsilyl ester of ethylphosphonic acid in which tin or silicon is attached to phosphorus through oxygen, for example:

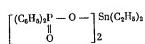


When the same tin derivative reacts with diethyl ethylphosphonate, the same product is obtained, its melting point being un depressed by admixture of the product of the reaction with the phosphorous ester. Only ethyl phosphonic acid was isolated from the hydrolysis products.

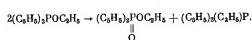
After checking the results of our previous investigations, we came to the conclusion that Malatesta's views are correct. We hydrolyzed a comparatively large amount of the substance obtained from the reagents given in equation (2b) and obtained a fairly good yield of ethylphenylphosphinic acid, the formation of which is in accord with the course of the reaction proposed by Malatesta and is in conflict with reaction according to the scheme of the Arbuzov rearrangement. When ethyl diphenylphosphinate was treated with a dialkytin diiodide, the product was similar to that of the reaction between diethyl phenylphosphonite and the same tin derivative.



In the case of the reaction of alkyltin halides with ethyl diphenylphosphonite, the Malatesta reaction, with formation of a product containing the P—O—Sn linkage, is impossible because the ester isomerizes into ethyl-diphenylphosphine oxide, which does not react with alkyltin halides. After careful purification of the products of the reaction between ethyl diphenylphosphonite and diethyltin dichloride, we concluded that the crystalline product has the structure:



and is formed from ethyl diphenylphosphonite present as impurity in the diphenylphosphonous ester or is formed as a result of an intramolecular oxidation-reduction reaction:



Experiments carried out in order to verify the possibility of such a change did not give positive results. An

attempt to oxidize ethyl diphenylphosphonite into vinyl diphenylphosphonate with oxygen was also unsuccessful.

EXPERIMENTAL

Action of Diethyltin Diiodide on Diethyl Ethylphosphonate. A mixture of 15.4 g (1 mole) of the iodide and 11.8 g (2 moles) of the ester was heated in a flask fitted with a condenser set for distillation. When the temperature of the solution was 125°, ethyl iodide began to distill over, the total amount collected being 8 g (72%). The residue in the flask solidified; the yield (16.9 g) was almost quantitative. Recrystallization from butyl alcohol did not affect the melting point (261–263°), and a mixture test with the substance obtained from the same iodide and triethyl phosphate showed no depression.

Action of Diethyltin Diiodide on Ethyl Ethylphenylphosphonate. Reaction was between 5.2 g (2 moles) of the ester and 5.7 g (1 mole) of the iodide. A solution of the tin compound in the ester was heated in a flask fitted with a condenser set for distillation, and the crystalline residue remaining after distillation of ethyl iodide was washed with a mixture of alcohol and ether. The yield was 5.3 g (78%), and the substance melted with decomposition at 292–294° (measured in a block). There was no depression in a mixture test with the product obtained from diethyl phenylphosphonite and diethyltin diiodide.

Hydrolysis. The substance (3 g) was dissolved in concentrated hydrochloric acid (40 ml). The solution was set aside for 48 hours at room temperature and was then evaporated down several times, first with hydrochloric acid, and then with water until the whole of the hydrochloric acid had been removed. The residue crystallized out, 1.8 g, m.p., 79–80° (from benzene). There was no depression of melting point in a mixture test with a sample of ethylphenylphosphinic acid obtained by the hydrolysis of ethyl ethylphenylphosphonate. Hydrolysis of the organic compound of tin and phosphorus obtained from the phosphorous ester also gave ethylphenylphosphinic acid.

Action of Diethyltin Dichloride on Ethyl Diphenylphosphonite. A mixture of 5.9 g (2 moles) of the ester and 3.18 g (1 mole) of the chloride was heated in an atmosphere of dry nitrogen until ethyl chloride ceased to be evolved; the maximum temperature attained by the solution was 210°. When cooled in a current of nitrogen, the reaction mass crystallized out. After being washed with alcohol and ether, the crystals melted at 346–349° (measured in a block).

Found %: C 54.67; H 5.09; 4.95
C₂₂H₁₈O₂P₂Sn. Calculated %: C 55.00; H 4.94

Ethyl diphenylphosphine oxide was isolated from the filtrate. When the substance was hydrolyzed with concentrated hydrochloric acid, almost quantitative yields were obtained of diphenylphosphinic acid, m.p., 192–194°, and diethyltin dichloride, m.p. 82–84°.

SUMMARY

On the basis of Malatesta's results and of our confirmatory experiments, it must be considered that the organic compounds of tin and phosphorus under consideration are esters of phosphorus acids in which tin is linked to phosphorus through oxygen.

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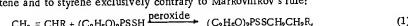
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 Kazan Affiliated Institute of the Academy
 of Sciences of the USSR

REACTION OF O,O-DIALKYL HYDROGEN PHOSPHORODITHIOATES
 WITH VINYL SULFIDES

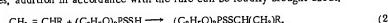
T. A. Mastryukova, E. N. Prilezhaeva, N. I. Uvarova,
 M. F. Shostakovsky, and M. I. Kabachnik

Addition reactions between O,O-dialkyl hydrogen phosphorodithioates and various unsaturated compounds have recently attracted much attention. As shown recently [1], O,O-dialkyl hydrogen phosphorodithioates are relatively strong acids ($K \approx 10^{-2}$), having ionization constants that are much higher than those of most thiols and their carboxylic acids. Moreover, these compounds are readily oxidized with the formation of compounds containing a disulfide bond [2]. This reaction, which is characteristic of all thiol compounds, indicates the ready formation of thiol radicals. It might be expected, therefore, that O,O-dialkyl hydrogen phosphorodithioates would readily add at double bonds, the mechanism of the reaction being either ionic or free-radical depending on the experimental conditions and the character of the unsaturated compound used. Correspondingly, addition products should be readily formed by reaction both in accordance with and also contrary to Markovnikov's rule.

In some of the papers that have been published on this matter, the structures of the addition products were not proved, in some cases it being assumed that addition proceeded contrary to the rule [3, 4, 5], and in others that it proceeded in accordance with the rule [6]. The question has been investigated in greater detail for the case of reaction between O,O-diethyl hydrogen phosphorodithioate and unsymmetrical olefins [7, 8]. The authors developed a reliable method for proving the structures of the resulting addition products by scission with sodium alkoxide, and they showed that, in the presence of a peroxide, pure O,O-diethyl hydrogen phosphorodithioate adds to 1-octene and to styrene exclusively contrary to Markovnikov's rule:



In absence of peroxides, addition in accordance with the rule can be readily brought about:

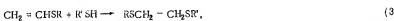


A catalyst for "normal" addition - which at the same time decomposes peroxides - is the sulfide P_2S_9 , which is present in undistilled O,O-diethyl hydrogen phosphorodithioate prepared from alcohol and phosphorus pentasulfide [7, 9]. The presence of this sulfide as impurity explains the "normal" addition of unpurified O,O-diethyl hydrogen phosphorodithioates to unsymmetrical olefins observed previously by the same authors [8].

It is probably because of their high acidity that O,O-dialkyl hydrogen phosphorodithioates, unlike thiols, have a high rate of uncatalyzed "normal" addition*. In this connection it was considered to be of interest to study the addition of O,O-dialkyl hydrogen phosphorodithioates to the double bond of vinyl sulfides. A study of the ionic reaction of the latter [11] showed that their double bond is somewhat less nucleophilic than that of the strongly nucleophilic vinyl ethers. Vinyl sulfides are however considerably more nucleophilic than unsymmetrical olefins. Nevertheless, some thiols, including benzenethiol, add so readily under normal conditions

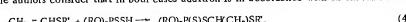
* In absence of peroxides, aliphatic thiols, benzenethiol, and thio carboxylic acids either do not add at all to olefins, or add extremely slowly [10].

to vinyl sulfides in the direction contrary to that required by Markovnikov's rule:



that the occurrence of this reaction forms a substantial obstacle in the synthesis of vinyl sulfides from thiols and acetylene [12-14]. In order to suppress "abnormal" addition of ethanethiol to ethyl vinyl sulfide, considerable amounts of antioxidant must be present. Under these conditions the thiol slowly reacts in accordance with Markovnikov's rule [13].

The reactions between O,O-dialkyl hydrogen phosphordithioates and vinyl sulfides and ethers are referred to in a patent [6]. The authors consider that in both cases addition is in accordance with Markovnikov's rule:

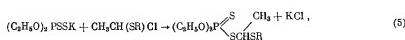


but they give no proofs of the structures of their products. Moreover, they do not give the constants of the products and do not indicate the degree of purity of the starting materials.

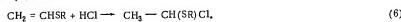
We have studied the addition of O,O-diethyl and -diisobutyl hydrogen phosphordithioates to a series of vinyl sulfides, namely, ethyl, butyl, and 2-butoxyethyl vinyl sulfides. All of the reagents were taken in the freshly distilled form, but no special precautions were taken to remove oxygen and traces of peroxides. The reactions were all exothermic, and the only products were O,O-diethyl 1-alkylthioethyl phosphordithioates which were isolated in 60-80% yield. Hence, addition occurred in accordance with Markovnikov's rule*. The addition of 0.7% of the active free-radical initiator 2,2'-azobis(2-methylpropionitrile) - which effects the abnormal addition of hydrogen sulfide and thiols to alkyl and aryl vinyl ethers [15] - did not affect the direction of the reaction.

All of the products (Table 1) are colorless oily liquids which are very readily superheated in the distillation process. They are readily soluble in various organic solvents. They are oxidized with difficulty by nitric acid.

In order to prove the structure of the products, O,O-diethyl S-1-ethylthioethyl and S-1-butylthioethyl phosphordithioates were synthesized by a different method which confirmed their structure, namely by the alkylation of potassium O,O-diethyl phosphordithioate with the corresponding alkyl 1-chloroethyl sulfide:



The required alkyl 1-chloroethyl sulfides were prepared by the hydrochlorination of vinyl ethers under the conditions described previously [11]:



The constants of the substances prepared by the two methods were in close agreement (Table 2).

As another method for proving the structure, the reaction with mercuric chloride in an ethanol medium was used. This reaction has been proposed previously for the quantitative determination of monothioacetals [17, 18] and symmetrical mercaptals [13, 19], which are split by the action of mercuric chloride with the elimination of one and two equivalents, respectively, of hydrogen chloride;

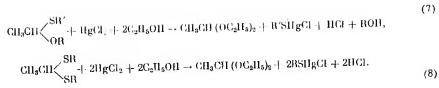
* It was established by a special experiment on the reaction between O,O-diethyl hydrogen phosphordithioate and ethyl vinyl sulfide that an O,O-dialkyl hydrogen phosphordithioate purified via a salt in accordance with Bacon and le Sueur's method [??] also adds to a vinyl sulfide in the direction required by Markovnikov's rule.

TABLE 1
O,O-Diethyl S-1-Alkylthioethyl Phosphordithioates

Formula of substance	B.p. in °C (p in mm)	n_D^{20}	ϵ_4^{20}	MR calculated	Yield (%)
$(\text{C}_2\text{H}_5\text{O})_2\text{P} \begin{array}{c} \diagdown \\ \text{S} \\ \diagup \end{array} \text{CH}_3 - \text{SC}_2\text{H}_5$	109-110 (2.5)	1.5290	1.1302	74.18	74.01
$(\text{C}_2\text{H}_5\text{O})_2\text{P} \begin{array}{c} \diagdown \\ \text{S} \\ \diagup \end{array} \text{CH}_3 - \text{SC}_2\text{H}_5$	109-110 (2)	1.5198	1.0965	83.84	83.25
$(\text{C}_2\text{H}_5\text{O})_2\text{P} \begin{array}{c} \diagdown \\ \text{S} \\ \diagup \end{array} \text{CH}_3 - \text{SC}_2\text{H}_5$	123-125 (3)	1.5125	1.0940	95.10	94.12
$(i\text{-C}_4\text{H}_9\text{O})_2\text{P} \begin{array}{c} \diagdown \\ \text{S} \\ \diagup \end{array} \text{CH}_3 - \text{SC}_2\text{H}_5$	113-115 (2)	1.5070	1.0556	93.18	93.49
$(i\text{-C}_4\text{H}_9\text{O})_2\text{P} \begin{array}{c} \diagdown \\ \text{S} \\ \diagup \end{array} \text{CH}_3 - \text{SC}_2\text{H}_5$	121-122 (2)	1.5052	1.0384	102.5	102.8
$(i\text{-C}_4\text{H}_9\text{O})_2\text{P} \begin{array}{c} \diagdown \\ \text{S} \\ \diagup \end{array} \text{CH}_3 - \text{SC}_2\text{H}_5$	124-126 (3)	1.5012	1.0422	113.8	112.6

TABLE 2
Specimens of O,O-Diethyl S-1-Alkylthioethyl Phosphordithioates Prepared by Two Different Methods

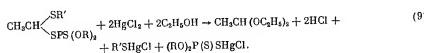
Formula of substance	Method of preparation	B.p. in °C (p in mm)	n_D^{20}	ϵ_4^{20}
$(\text{C}_2\text{H}_5\text{O})_2\text{P} \begin{array}{c} \diagdown \\ \text{S} \\ \diagup \end{array} \text{CH}_3 - \text{SC}_2\text{H}_5$	By addition By alkylation of salt	109-110 (2.5) 109-110 (2.5)	1.5290 1.5289	1.1392 1.1391
$(\text{C}_2\text{H}_5\text{O})_2\text{P} \begin{array}{c} \diagdown \\ \text{S} \\ \diagup \end{array} \text{CH}_3 - \text{SC}_2\text{H}_5$	By addition By alkylation of salt	109-110 (2) 109-110 (2)	1.5198 1.5290	1.0965 1.0969



(8)

Owing to the low alcohol-solubility of the alkylthiomercury chlorides formed, the reaction goes practically to completion. The isomeric ethers of 2-mercaptoethanol and 1,2-ethanedithiol give the complex salts usually obtained from sulfides when treated with mercuric chloride, and no hydrogen chloride is eliminated [13, 17].

The products of the addition of O,O-dialkyl hydrogen phosphorodithioates to vinyl sulfides behave toward mercuric chloride in an alcoholic medium as members of a series of phosphorus-containing mercaptals, yielding two equivalents of hydrogen chloride and decomposing according to the equation:



In the scission of O,O-diethyl S-1-ethylthioethyl phosphorodithioate with alcoholic mercuric chloride, by-products corresponding to the above equation were detected. Ethylthiomercury chloride was isolated, yield dichloric acid and a carboxaldehyde diethyl acetal were titrated quantitatively. The acetaldehyde obtained by hydrolysis of the acetal was identified as its dimethylphenylhydrazone. As regards the chloromercury O,O-diethyl phosphorodithioate, we did not succeed in isolating it in the pure state owing to the occurrence of disproportionation during recrystallization:



Mercury bis(O,O-diethyl phosphorodithioate) was isolated and identified. Chloromercury O,O-diethyl phosphorodithioate prepared in a known way also underwent the same disproportionation when recrystallized.

The specimens of O,O-diethyl S-1-alkylthioethyl phosphorodithioates prepared by the two methods reacted in identical manner with alcoholic mercuric chloride.

EXPERIMENTAL

Freshly distilled reactants were used in the experiments. The alkyl vinyl sulfides were prepared from thiols and acetylene [12, 13, 20], and the O,O-diethyl hydrogen phosphorodithioates were prepared from phosphorus pentasulfide and alcohols and were purified by vacuum fractionation [2, 21].

Preparation of O,O-Dialkyl S-1-Alkylthioethyl Phosphorodithioates

In all of the experiments the O,O-dialkyl hydrogen phosphorodithioate was added dropwise with stirring to a slight excess of the vinyl sulfide, the rate of addition being such that the temperature of the reaction mixture was maintained within the range 60–62°. When addition was complete, the temperature rapidly fell to that of the room. The mixture was stirred for a further 30 minutes and was set aside overnight. It was then vacuum-fractionated.

O,O-Diethyl S-1-Ethylthioethyl Phosphorodithioate. This was prepared from 6.0 g (0.068 mole) of ethyl vinyl sulfide and 9.3 g (0.05 mole) of O,O-diethyl hydrogen phosphorodithioate; b.p. 109–110° (2.5 mm); n_D^{20} 1.5290; d_4^{20} 1.1395; yield 10.0 g (73%).

Found %: C 34.78; 34.87 II 6.84; 7.00; P 11.05; 11.37
 $C_{10}\text{H}_{19}\text{O}_2\text{PS}_2$. Calculated %: C 35.01 II 6.98; P 11.29

Found: MR 73.18

Calculated: MR 74.01

O,O-Diethyl S-1-Butylthioethyl Phosphorodithioate. This was prepared from 9.0 g (0.078 mole) of butyl vinyl sulfide and 14.3 g (0.077 mole) of O,O-diethyl hydrogen phosphorodithioate; b.p. 109–110° (2 mm); n_D^{20} 1.5198; d_4^{20} 1.0965; yield 15.5 g (66.2%).

Found %: P 10.64; 10.64

$C_{12}\text{H}_{23}\text{O}_2\text{PS}_2$. Calculated %: P 10.25

Found: MR 83.84

Calculated: MR 83.25

O,O-Diethyl S-1-(2-Butoxyethylthio)ethyl Phosphorodithioate. This was prepared from 10.0 g (0.062 mole) of 2-butoxyethyl vinyl sulfide and 11.0 g (0.058 mole) of O,O-diethyl hydrogen phosphorodithioate; b.p. 123–125° (3 mm); n_D^{20} 1.5125; d_4^{20} 1.0940; yield 16.3 g (90%).

Found %: C 41.52; 41.64; H 7.84; 7.87; P 8.88; 9.07

$C_{14}\text{H}_{27}\text{O}_2\text{PS}_2$. Calculated %: C 41.59; H 7.86; P 8.94

Found: MR 85.10

Calculated: MR 94.12

O,O-Diisobutyl S-1-Ethylthioethyl Phosphorodithioate. This was prepared from 6.0 g (0.068 mole) of ethyl vinyl sulfide and 10.5 g (0.044 mole) of O,O-diisobutyl hydrogen phosphorodithioate; b.p. 113–115° (2 mm); n_D^{20} 1.5070; d_4^{20} 1.0556; yield 11.0 g (77.5%).

Found %: C 43.43; 43.20; H 8.18; 8.15; P 9.40; 9.51

$C_{12}\text{H}_{23}\text{O}_2\text{PS}_2$. Calculated %: C 43.59; H 8.48; P 9.30

Found: MR 93.18

Calculated: MR 93.49

O,O-Diisobutyl S-1-Butylthioethyl Phosphorodithioate. This was prepared from 6.0 g (0.051 mole) of butyl vinyl sulfide and 10.5 g (0.044 mole) of O,O-diisobutyl hydrogen phosphorodithioate; b.p. 121–122° (2 mm); n_D^{20} 1.5032; d_4^{20} 1.0884; yield 13.0 g (91.3%).

Found %: C 47.11; 47.11; H 8.99; 8.86; P 8.82; 8.83

$C_{14}\text{H}_{29}\text{O}_2\text{PS}_2$. Calculated %: C 46.91; H 8.69; P 8.64

Found: MR 102.5

Calculated: MR 102.8

O,O-Diisobutyl S-1-(2-Butoxyethylthio)ethyl Phosphorodithioate. This was prepared from 5.8 g (0.036 mole) of 2-butoxyethyl vinyl sulfide and 7.0 g (0.029 mole) of O,O-diisobutyl hydrogen phosphorodithioate; b.p. 124–126° (3 mm); n_D^{20} 1.5012; d_4^{20} 1.0422; yield 9.0 g (78.2%).

Found %: C 47.49; 47.68; H 8.79; 8.75; P 7.84; 7.86

$C_{16}\text{H}_{35}\text{O}_2\text{PS}_2$. Calculated %: C 47.71; H 8.76; P 7.70

Found: MR 111.8

Calculated: MR 112.6

Synthesis of O,O-Dialkyl S-1-Alkylthioethyl Phosphorodithioates from Alkyl 1-Chloroethyl Sulfides.

Preparation of O,O-Diethyl S-1-Ethylthioethyl Phosphorodithioate. In a flask fitted with stirrer, 11.2 g (0.09 mole) of 1-chloroethyl ethyl sulfide was added dropwise to 11.2 g (0.05 mole) of potassium O,O-diethyl phosphorodithioate suspended in 25 ml of dry ether. The temperature rose to 35° and the ether boiled. The reaction was heated in a water bath at 40° for three hours. The precipitate of potassium chloride was filtered off (3.98 g; the theoretical amount was 3.72 g). The filtrate was dried over calcined sodium sulfate and vacuum-fractionated; b.p. 109–110° (2.5 mm); n_D^{20} 1.5289; d_4^{20} 1.1391; yield 8.5 g (62%); found MR 74.30; calculated for $C_{10}\text{H}_{19}\text{O}_2\text{PS}_2$ MR 74.01.

Preparation of O,O-Diethyl S-1-Butylthioethyl Phosphorodithioate. This was prepared in a similar way from 8.0 g (0.05 mole) of butyl 1-chloroethyl sulfide and 11.2 g (0.05 mole) of potassium O,O-diethyl phosphorodithioate in 20 ml of absolute ether. b.p. 109-110° (2 mm); n_D²⁰ 1.8200; u_d²⁰ 1.0969; yield 10.8 g (71%); found MR 83.82; calculated for C₁₀H₁₈O₂PS₂ MR 83.25.

Reaction of O,O-Dialkyl S-1-Alkylthioethyl Phosphorodithioates with Mercuric Chloride

Reaction of O,O-Diethyl S-1-Ethylthioethyl Phosphorodithioate with Mercuric Chloride. A solution of 9.2 g (0.081 mole) of mercuric chloride in 11 ml of 96% ethanol was added to 1 g (0.0038 mole) of O,O-diethyl S-1-ethylthioethyl phosphorodithioate. The white precipitate that quickly formed was filtered off after three hours and washed with cold alcohol. The alcohol was added to the filtrate, and the precipitate was vacuum-dried (weight 1.8 g). After the filtrate had stood for five days, a further 0.15 g of crystals came down. Titration of part of the filtrate with standard caustic soda solution gave a hydrochloric acid content of 97.7% of the theoretical value. The filtrate was evaporated to dryness at a residual pressure of 10 mm, the distillate being collected in a trap cooled with dry ice and acetone. Determination of acetylaldehyde diethyl acetate in part of the distillate by the hydroxylamine method gave 92.9% of the theoretical value. To the remaining part of the distillate, 0.45 g of diisopropenylhydrazine and 0.5 ml of concentrated hydrochloric acid were added; the mixture was boiled for 30 minutes and then cooled, when golden needles of a tetraldehyde dinitrophenylhydrazone came down (m.p., after recrystallization 163-164°). The weight of the dry residue remaining after the distillation was 0.6 g, reduced to 0.3 g after treatment with water to remove unchanged mercuric chloride. The residue was not treated further since it rapidly turned black. The total weight of mercury salts isolated was 2.25 g (theory requires 2.6 g).

The salts that came down from the solution (1.95 g) were extracted several times with boiling alcohol (75 ml in all). The weight of the residue that remained undissolved was 0.8 g. Recrystallization from boiling xylene [22] gave nearly leaves, which did not melt, but gradually decomposed above 250°.

Found %: C 8.40; 8.47; H 1.82; 2.09
Calculated %: C 8.08; H 1.68

When cooled, the alcohol yielded 0.7 g of fine crystals, which were heated with boiling benzene for one hour in order to complete disproportionation. The decomposition temperature of the crystals that separated from the benzene was 121-121.5°. In admixture with known mercury bis[O,O-diethyl phosphorodithioate] (see below) it melted with decomposition at 121-122°.

Found %: C 16.43; 16.57; H 3.61; 3.40
Calculated %: C 16.82; H 3.53

Preparation of Chloromercury O,O-Diethyl Phosphorodithioate (C₁₀H₁₈O₂)₂PSSHgCl. An aqueous solution of 13.6 g (0.06 mole) of mercuric chloride was added to an aqueous solution of 11.2 g (0.05 mole) of potassium O,O-diethyl phosphorodithioate. There was an immediate white precipitate, which was filtered off, washed with a large amount of water, and dried. It melted with decomposition at 126-127°; the yield was quantitative.

Found %: C 11.07; 11.72; H 2.83; 2.50
Calculated %: C 11.40; H 2.45

After two recrystallizations from benzene the substance melted at 122-123°, but the carbon and hydrogen contents were greatly increased. After five recrystallizations from benzene the substance had m.p. 121-122° and its composition corresponded to complete disproportionation.

Found %: C 16.63; 16.41; H 3.46; 3.40
Calculated %: C 16.82; H 3.53

Preparation of Mercury Bis(O,O-diethyl phosphorodithioate). An aqueous solution of 5.6 g (0.025 mole) of potassium O,O-diethyl phosphorodithioate was added to an aqueous solution of 3.4 g (0.013 mole) of mercuric chloride. A voluminous white precipitate of the mercury compound formed, was filtered off, washed with water, and dried. The yield was quantitative. After being recrystallized from ben-

zeno; it melted with decomposition at 121-122°.

Found %: C 16.48; 16.80; H 3.50; 3.55
Calculated %: C 16.82; H 3.53

TABLE 3
Titration of O,O-Dialkyl S-1-Alkylthioethyl Phosphorodithioates (RO)₂PSSC(CH₂)SR

R	R'	Method of preparation	Equivalent		Content of eliminable S (%)	
			found	calc.	found	calc.
C ₂ H ₅	C ₂ H ₅	Addition of distilled O,O-hydrogen phosphorodithioate to ethyl vinyl sulfide	140.8	137.22	23.91	23.37
C ₂ H ₅	C ₂ H ₅	Ditro, but with purification of the O,O-diethyl hydrogen phosphorodithioate via the salt [7]	135.2	137.22	23.02	23.37
C ₂ H ₅	C ₂ H ₅	Alkylation of potassium O,O-diethyl phosphorodithioate with 1-chloroethyl ethyl sulfide	137.3	137.22	23.38	23.37
C ₂ H ₅	C ₄ H ₉	Addition	135.9	137.22	23.09	23.37
C ₂ H ₅	C ₄ H ₉	Addition	150.4	151.25	21.09	21.20
C ₂ H ₅	C ₄ H ₉	Alkylation	148.7	151.25	20.87	21.20
C ₂ H ₅	C ₄ H ₉	Addition	149.8	151.25	20.99	21.20
C ₂ H ₅	CH ₂ Cl ₂ OC ₂ H ₅	Addition	172.5	173.26	18.13	18.20
i-C ₄ H ₉	C ₂ H ₅	Addition	171.4	173.26	17.96	18.20
i-C ₄ H ₉	C ₂ H ₅	Addition	164.3	165.25	19.30	19.40
i-C ₄ H ₉	C ₂ H ₅	Addition	155.4	165.25	19.55	19.65
i-C ₄ H ₉	C ₂ H ₅	Addition	178.4	179.25	17.84	17.93
i-C ₄ H ₉	CH ₂ Cl ₂ OC ₂ H ₅	Addition under usual conditions	177.5	179.25	17.75	17.85
i-C ₄ H ₉	CH ₂ Cl ₂ OC ₂ H ₅	Addition in presence of 0.1% of 2,2'-azobis(2-methylpropionitrile)	203.4	201.3	16.09	16.93
i-C ₄ H ₉	CH ₂ Cl ₂ OC ₂ H ₅	Addition in presence of 0.1% of 2,2'-azobis(2-methylpropionitrile)	201.1	201.3	16.07	15.93
i-C ₄ H ₉	CH ₂ Cl ₂ OC ₂ H ₅	[azobis(2-methylpropionitrile)]	201.7	201.7	15.94	15.94

Quantitative Determination of O,O-Dialkyl S-1-Alkylthioethyl Phosphorodithioates

The titration was carried out as already described for monothioacetals [17] and vinyl sulfides [12]. A weighed amount (0.0005-0.001 mole) of O,O-dialkyl S-1-alkylthioethyl phosphorodithioate was placed in a conical flask, and 5-6 times as much (in moles) of mercuric chloride was added as a 20% solution in ethanol. After 1-2 hours the acid liberated was titrated with 0.1 N NaOH to a yellow color with methyl orange. It was found necessary to shake the precipitate well during the titration in order to avoid the formation of mercuric oxide.

The calculated equivalents on the basis of equation (9) and the contents of eliminable sulfur are given in Table 3.

SUMMARY

1. It was shown that O,O-dialkyl hydrogen phosphorodithioates readily add to vinyl sulfides in accordance with Markovnikov's rule.

2. A series of O,O-dialkyl S-1-alkylthioethyl phosphorodithioates were prepared. Their structure was proved by two methods: synthesis from alkyl 1-chloroethyl sulfides, and scission by means of mercuric chloride in ethanol.

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* T.p. = C. B. Translation pagination.

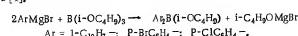
ORGANOBORON COMPOUNDS

COMMUNICATION 8. SYNTHESIS AND PROPERTIES OF DIARYLBORONIC ACIDS

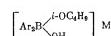
B. M. Mikhailov and V. A. Vaver

In a previous paper [1] we have described the preparation of diphenylboronic acid and its derivatives. The properties of these compounds and the desire to correct some inaccuracies in data reported in the literature for some other diarylboric acids prompted us to synthesize a few more representatives of this class of compounds.

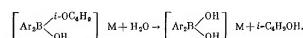
We prepared di-1-naphthyl-, bis-p-bromophenyl-, and bis-p-chlorophenyl-boronic acids. The isobutyl esters of these acids were isolated in 40-63% yield, together with the corresponding dibutyl aranobonates, from the reaction products obtained by heating two equivalents of arylmagnesium bromide with one equivalent of triisobutyl borate. The reactions were carried out under the same conditions as those used in the synthesis of isobutyl diphenylboronate [1].



A characteristic property of these diarylboric esters is their stability to hydrolysis by water and dilute mineral acids. A second peculiarity is their ability to dissolve in caustic alkalis with formation, as in the case of isobutyl diphenylboronate [1], of salts of diaryldihydroxyboron acids*:



When aqueous solutions of such salts are heated, the alkoxy group of the anion is hydrolyzed with formation of a salt of diaryldihydroxyboric acid:

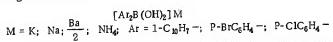


Barium salts of diaryldihydroxyboric acids are readily prepared by direct treatment of diarylboric esters with saturated barium water. It is probable that in this case the same hydrolysis reaction occurs with the anion of the barium salt of the alkoxydihydroxyboric acid, which is formed in the first place, but it proceeds more rapidly as a result of the poor solubility in water of barium salts of diaryldihydroxyboric acids.

* As there is no recognized system of nomenclature for compounds of this type, they are named here by an adaptation of the nomenclature for inorganic complex compounds, "organic" names, however, being given for radicals (e.g. hydroxy, not hydroxo). - Publisher.

Di-1-naphthyl- and bis-p-bromophenyl-boronic esters react readily also with aqueous ammonia, ammonium salts of the corresponding diaryldihydroxyboric acids being formed. Bis-p-chlorophenylborinic esters are unexceptional in this respect; they do not react with aqueous ammonia, neither at room temperature nor when heated.

When salts of general formula



are treated with acid, they are converted into acids. Salts of dihydroxydi-1-naphthyl- and bis-p-bromophenyl-dihydroxy-boric acid give the corresponding diarylborinic acid, but salts of bis-p-chlorophenyl-dihydroxy-boric acid, like those of the corresponding diphenyl compound, give a monohydrate of the diarylborinic acid.

Unlike diarylborinic acid, the diarylborinic acids now prepared do not form anhydrides when heated in a vacuum, but are converted under these conditions into areneneboronic acids with elimination of one aryl radical. Anhydrides can be prepared by treating the acids with thionyl chloride, this being demonstrated for the case of di-1-naphthylborinic acid:



In conclusion, we must discuss data reported in the literature on the diarylborinic acids that we have prepared. Di-1-naphthylborinic acid was isolated recently by Letzinger and coworkers [2], who obtained it by acid hydrolysis of its amine borane ester. As regards the bis-p-bromophenyl- and bis-p-chlorophenyl-borinic acids described by König and Scharinbeck [3] and by Melnikov and Rokitskaya [4], it is clear from the methods used that the authors could not have isolated these substances.

König and Scharinbeck, and later Melnikov and Rokitskaya, prepared their organoboron compounds by reaction between equivalent amounts of arylmagnesium bromide and tributyl borate. After treatment of the reaction products with dilute acid and separation of areneneboronic acid, the best the residue could contain a diarylborinic ester, which is not hydrolyzed under these conditions, but it could not contain a diarylborinic acid.

For bis-p-bromophenylborinic acid, König and Scharinbeck give m.p. 113°, whereas the acid actually melts at 91°. According to Melnikov and Rokitskaya's results, bis-p-chlorophenylborinic acid corresponds in composition to $(\text{C}_6\text{H}_5\text{H}_2)_2\text{B}(\text{OH})_2$, whereas its actual composition corresponds to $(\text{C}_6\text{H}_5\text{H}_2)_2\text{B}(\text{OH})\text{H}_2\text{O}$. Moreover, Melnikov and Rokitskaya state, incorrectly, that reaction between equimolecular amounts of tributyl borate and p-chlorophenylmagnesium bromide gives bis-p-chlorophenylborinic acid in 17% yield together with a smaller amount of p-chlorobenzeneboronic acid (15%). We repeated Melnikov and Rokitskaya's experiments and showed that, under their conditions, only p-chlorobenzeneboronic acid is obtained and no bis-p-chlorophenylborinic ester is formed.

EXPERIMENT

Isobutyl Di-1-naphthylborinate. With vigorous mechanical stirring, a solution of 0.225 mole (52 g) of tributyl borate in 50 ml of absolute ether was added over a period of 15 minutes to 0.5 mole of 1-naphthylmagnesium bromide as a molar solution in a mixture of ether and benzene, the temperature being maintained at -60° to -30°. When addition of the boric ester was complete, the temperature was lowered, -70° to -75°, and the reaction mixture stirred at this temperature for 6-7 hours. The next day the reaction products were treated with 850 ml 5% HCl. The ether-benzene layer was separated, and the aqueous layer was extracted with ether. The combined ether-benzene extracts were dried with calcined sodium sulfate. After distilling off solvents, a yellowish viscous residue remained; after dilution with 50 ml isopentane, this solidified into a crystalline mass. The reaction product was filtered off under suction, thoroughly washed with isopentane, and vacuum-dried. The product, amounting to 47.6 g (63%) was iso-butyl di-1-naphthylborinate, m.p. 104-105° (after recrystallization from hexane).

Found %: C 85.20; 85.14; H 6.73; 6.77; B 3.17; 3.24
 $\text{C}_{18}\text{H}_{22}\text{BO}$. Calculated %: C 85.22; H 6.85; B 3.19

Distillation of solvent from the isopentane filtrate and esterification of the residue with iso-butyl alcohol resulted in the isolation of 10 g (15%) of iso-butyl 1-naphthaleneboronate, b.p. 166-168° (6 mm) and d_4^{25} 0.9777.

Found %: $\text{C}_{12}\text{H}_{16}$ 43.70; 43.84; B 3.60; 3.67

$(\text{C}_{12}\text{H}_{16})\text{B}(\text{OC}_4\text{H}_9)_2$. Calculated %: $\text{C}_{12}\text{H}_{16}$ 44.42; B 3.78

Iso-butyl di-1-naphthylboronate is a colorless crystalline substance, readily soluble in benzene and chloroform, difficultly soluble in petroleum ether and methanol, and insoluble in isopentane. Iso-butyl 1-naphthaleneboronate is a colorless liquid, readily hydrolyzed - even by atmospheric moisture - into 1-naphthaleneboronic acid.

Ammonium Dihydroxydi-1-naphthylborate. A suspension of 10 g of iso-butyl di-1-naphthylboronate in 50 ml of methanol was prepared and was stirred vigorously while 15 ml of 30% aqueous ammonia was added. At first the precipitate dissolved completely, and then a colorless crystalline substance was rapidly precipitated. The mixture was stirred for 30 minutes, and the reaction product was then filtered off at the pump, washed with methanol, and vacuum-dried to constant weight. The product, amounting to 8.85 g (97.5%), was ammonium dihydroxydi-1-naphthylborate, m.p. 105-107°. After recrystallization from methanol the substance melted at 107-108°.

Found %: $\text{C}_{12}\text{H}_{16}$ 19.44; 19.84; B 3.34; 3.20; N 4.12; 4.09

$(\text{C}_{12}\text{H}_{16})\text{B}(\text{OH})_2\text{NH}_4$. Calculated %: $\text{C}_{12}\text{H}_{16}$ 18.07; B 3.41; N 4.41

Ammonium dihydroxydi-1-naphthylborate is a colorless crystalline substance, readily soluble in benzene and hot methanol, difficultly soluble in cold methanol, and insoluble in water. In the air it rapidly decomposes with formation of 1-naphthaleneboronic acid and separation of ammonia and naphthalene.

Di-1-naphthylborinic Acid. A suspension of 4.94 g of ammonium dihydroxydi-1-naphthylborate was prepared in 30 ml of ether, and it was stirred vigorously while 5 ml of dilute (1:1) hydrochloric acid was added (acid reaction to Congo red). The ether layer was separated, and the remaining solution was extracted with ether. Ether was removed from the combined extracts under reduced pressure, and the residue was heated at 70° for 10-15 minutes. The reaction product was dissolved in a little dry benzene and reprecipitated with 50 ml of isopentane. The product, amounting to 3.15 g (71.7%), was di-1-naphthylborinic acid, m.p. 113-114°. After being recrystallized from petroleum ether, the di-1-naphthylborinic acid melted at 114.5-115°.

Found %: C 84.83; 84.90; H 5.26; 5.38; B 3.91; 3.97

$(\text{C}_{12}\text{H}_{16})_2\text{BO}(\text{C}_6\text{H}_5)_2$. Calculated %: C 85.13; H 5.35; B 3.83

Di-1-naphthylborinic acid is a colorless crystalline substance, readily soluble in benzene, difficultly soluble in petroleum ether, and insoluble in isopentane. When it is heated above its melting point in a vacuum, no anhydride formation occurs, but elimination of one of the naphthyls as naphthalene slowly occurs with formation of 1-naphthaleneboronic acid.

Di-1-naphthylborinic Anhydride. A solution of 2 g of di-1-naphthylborinic acid in 5 ml of thionyl chloride was refluxed for two hours. Thionyl chloride was removed under reduced pressure, and the residue was crystallized from a mixture of benzene and petroleum ether. The product, amounting to 1.9 g (96%), was di-1-naphthylborinic anhydride, m.p. 180-182°.

Found %: $\text{C}_{12}\text{H}_{16}$ 91.80; 91.96; B 4.24; 4.20

$(\text{C}_{12}\text{H}_{16})_2\text{BO}(\text{C}_6\text{H}_5)_2$. Calculated %: $\text{C}_{12}\text{H}_{16}$ 92.08; B 4.34

Di-1-naphthylborinic anhydride is a colorless crystalline substance, difficultly soluble in benzene and insoluble in petroleum ether and isopentane.

Iso-butyl Bis-p-bromophenylborinate. With vigorous mechanical stirring, a solution of 0.25 mole of tributyl borate in 100 ml of absolute ether was added over a period of 30 minutes to 0.65 mole of p-bromophenylmagnesium bromide as a molar etheral solution (prepared by Pink's method [5]), the temperature being maintained at -30° to -60°. The reaction mixture was stirred at -70° to -75° for eight hours. The reaction products were treated with 450 ml of 5% hydrochloric acid. The residue remaining after removal of ether was esterified with 25 ml of iso-butyl alcohol and vacuum-fractionated from a Claisen flask in a current of dry nitrogen. Two fractions were collected, b.p. 102-158° and 158-164° (1 mm) respectively. Further frac-

tionation of the reaction products yielded 38.0 g (39%) of isobutyl bis-p-bromophenylborinate, b.p. 161°-163° (1 mm), and 30 g (37%) of disisobutyl p-bromobenzeneboronate, b.p. 109°-110° (1 mm) and d_4^{25} 1.1583.

Found %: Br₂C₆H₄ 78.73; 78.60; B 2.65; 2.75

(BrC₆H₄)₂B(OC₄H₉)₂. Calculated %: Br₂C₆H₄ 78.80; B 2.73

Found %: Br₂C₆H₄ 49.72; 49.81; B 3.27; 3.31

(BrC₆H₄)₂B(OC₄H₉)₂. Calculated %: Br₂C₆H₄ 49.83; B 3.46

Isobutyl bis-p-bromophenylborinate is a colorless, very viscous substance, which slowly solidifies at room temperature. It is soluble in most organic solvents, and it slowly oxidizes in the air. Disisobutyl p-bromobenzeneboronate is a colorless liquid, which is very rapidly hydrolyzed when exposed to the atmosphere with formation of p-bromobenzeneboronic acid.

Ammonium Bis-p-bromophenylidihydroxyborate. Isobutyl bis-p-bromophenylborinate (2.25 g) and 30% aqueous ammonia (5 ml) were shaken together. The crystalline precipitate formed was filtered off at the pump, washed with water, and vacuum-dried to constant weight. The product, amounting to 1.85 g (87.3%), was ammonium bis-p-bromophenylidihydroxyborate, m.p. 133°-135°, unchanged by recrystallization from benzene.

Found %: Br₂C₆H₄ 83.58; 83.42; B 2.20; 2.21; N 3.64; 3.65

(BrC₆H₄)₂B(OH)₂NH₄. Calculated %: Br₂C₆H₄ 83.23; B 2.28; N 3.74

Ammonium bis-p-bromophenylidihydroxyborate is a colorless, odorless crystalline substance, soluble in methanol and ethanol, sparingly soluble in benzene, and insoluble in isopentane.

Potassium Bis-p-bromophenylidihydroxyborate. Isobutyl bis-p-bromophenylborinate (1.23 g) was dissolved in an equivalent amount of aqueous caustic potash (3.65 ml of 0.8 N solution), and water was then slowly distilled off in a current of nitrogen under reduced pressure at 60°-70°. The residue was a colorless crystalline substance. After recrystallization from a mixture of benzene with some methanol, 0.8 g was obtained.

Found %: Br₂C₆H₄ 78.56; 78.67; B 2.71; 2.73; K 9.81; 9.84

(BrC₆H₄)₂B(OH)₂K. Calculated %: Br₂C₆H₄ 78.80; B 2.73; K 9.87

Potassium bis-p-bromophenylidihydroxyborate is extremely soluble in water and alcohols, but insoluble in benzene, petroleum ether, and isopentane. It is converted quantitatively into bis-p-bromophenylborinic acid by treatment with dilute acids.

Bis-p-bromophenylborinic Acid. Ammonium bis-p-bromophenylidihydroxyborate (1.65 g) was treated with dilute hydrochloric acid. The reaction product was extracted with ether. After removal of ether, the residue was diluted with a little isopentane. The product, amounting to 1.30 g (85%) was bis-p-bromophenylborinic acid. After being washed from petroleum ether the acid melted at 90°-91°.

Found %: C 42.61; 42.69; H 2.83; 2.66; B 3.18; 3.17; Br 47.38; 47.10

C₂H₅BOBr₂. Calculated %: C 42.41; H 2.67; B 3.18; Br 47.03

Bis-p-bromophenylborinic acid is a colorless crystalline substance, readily soluble in alcohols and benzene, difficultly soluble in petroleum ether, and insoluble in isopentane. It can be prepared also from potassium bis-p-bromophenylidihydroxyborate (0.99 g of the potassium salt gave 0.760 g of acid, m.p. 87°-89°, when acidified); the melting point of a mixture with the analyzed sample of bis-p-bromophenylborinic acid was 89°-90°.

Isobutyl Bis-p-chlorophenylborinate. With vigorous stirring, a solution of 0.25 mole of tri-isobutyl borate in 100 ml of absolute ether was added over a period of 30 minutes to 0.6 mole of p-chlorophenylmagnesium bromide as a molar ethereal solution, the temperature being maintained at -30° to -60°. The reaction mixture was then cooled to a temperature of -70° to -75°, and it was stirred at this temperature for 8-9 hours. On the next day the reaction products were treated with 450 ml of 5% hydrochloric acid. The residue remaining after removal of ether from the combined extracts was esterified with 25 ml of isobutyl alcohol, the alcohol was distilled off, and the residue was distilled rapidly from a Claisen flask (in a current of nitrogen). Two fractions were collected: 70°-145° and 145°-155° (2 min). Further fractionation of the reac-

tion products through a Compel column in a current of nitrogen gave 31 g (40%) of isobutyl bis-p-chlorophenylborinate, b.p. 134°-135° (1 mm) and d_4^{25} 1.0051.

Found %: ClC₆H₄ 72.66; 72.23; B 3.55; 3.58; Cl 23.27; 23.31

(ClC₆H₄)₂B(OC₄H₉)₂. Calculated %: ClC₆H₄ 72.66; B 3.52; Cl 22.80

Found %: ClC₆H₄ 41.34; 41.09; B 3.90; 4.09

(ClC₆H₄)₂B(OC₄H₉)₂. Calculated %: ClC₆H₄ 41.33; B 4.03

Isobutyl bis-p-chlorophenylborinate is a very viscous colorless liquid, it is immiscible with water, but is soluble in most organic solvents. It is rapidly oxidized in the air. Disisobutyl p-chlorobenzeneboronate is a colorless mobile liquid, miscible with most organic solvents. It is immediately hydrolyzed in the atmosphere with formation of p-chlorobenzeneboronic acid,

Barium Bis-p-chlorophenylidihydroxyborate. Isobutyl bis-p-chlorophenylborinate (1.73 g) was shaken for 5-10 minutes with 15 ml of barium water (saturated at room temperature). The voluminous precipitate that formed after a few minutes was filtered off at the pump, washed with water, and dried to constant weight. The yield was 1.7 g (89.5%). Barium was determined by heating a weighed sample of the substance with INH₂SO₄, the excess of acid being then titrated with IN NaOH. Boron and chlorophenyl groups were determined in the usual way on a separate sample.

Found %: Ba 20.24; 20.26; ClC₆H₄ 65.59; 65.92; B 3.14; 3.09

(ClC₆H₄)₂B(OC₄H₉)₂Ba. Calculated %: Ba 20.40; ClC₆H₄ 66.20; B 3.21

Barium bis-p-chlorophenylidihydroxyborate is a colorless crystalline substance. It is insoluble in water, benzene, and isopentane, but readily soluble in methanol and ethanol. When treated with dilute hydrochloric acid it is converted into bis-p-chlorophenylborinic acid,

Bis-p-chlorophenylborinic Acid. Barium bis-p-chlorophenylidihydroxyborate (2.0 g) was shaken with 10 ml of dilute hydrochloric acid (1: 4). The emulsion that was immediately formed rapidly turned into a precipitate of a colorless crystalline substance, which was filtered off at the pump, washed with water, and dried over calcium chloride. The substance obtained (1.1 g; m.p. 76°-78° after reprecipitation by water from alcohol) corresponded in analysis to the monohydrate of bis-p-chlorophenylborinic acid. When dried in a vacuum it decomposed with elimination of chlorobenzene and formation of p-chlorobenzeneboronic acid,

Found %: C 54.53; 54.29; H 4.49; 4.28; B 4.08; 3.83; Cl 26.36; C₁₂H₁₁BO₂Cl₂. Calculated %: C 53.58; H 4.12; B 4.02; Cl 26.36

The monohydrate of bis-p-chlorophenylborinic acid is readily soluble in benzene, methanol, and ethanol, but insoluble in water.

Sodium Bis-p-chlorophenylidihydroxyborate. Isobutyl bis-p-chlorophenylborinate (2.84 g) was dissolved in the equivalent amount of caustic soda (8.4 ml of 1.09% NaOH). The solution was heated to 60°-70°, and water was slowly distilled off under reduced pressure. The residue was washed with benzene and vacuum-dried (yield 2.2 g).

Found %: Na 7.42; 7.65; B 3.53; 3.60

C₁₂H₁₁BO₂Cl₂Na. Calculated %: Na 7.90; B 3.72

Sodium bis-p-chlorophenylidihydroxyborate is very readily soluble in water and alcohols, but is insoluble in benzene, petroleum ether, and isopentane. On acidification it gives the monohydrate of bis-p-chlorophenylborinic acid, m.p. 72°-76° (0.3 g of the salt gave 0.25 g of the monohydrate). A mixture of the product with the analyzed sample of bis-p-chlorophenylborinic acid monohydrate melted at 72°-76°.

Boron and aryl groups were determined by Witting's method [6].

SUMMARY

1. The isobutyl esters of di-1-naphthyl-, bis-p-bromophenyl-, and bis-p-chlorophenyl-borinic acids were prepared.

2. It was shown that, when the isobutyl esters of di-1-naphthyl-, bis-p-bromophenyl-, and bis-p-chloro-

phenyl-boronic acids were treated with aqueous solutions of caustic soda, caustic potash, ammonia, and barium hydroxide, salts of the corresponding diaryldihydroxyboric acids were formed.

3. Di-1-naphthyl-, bis-p-bromophenyl, and bis-p-chlorophenyl-boronic acids were prepared by treating salts of di-1-naphthyl-, bis-p-bromophenyl-, and bis-p-chlorophenyl-dihydroxyboric acids with dilute hydrochloric acid.

4. It was shown that data reported in the literature for bis-p-bromophenyl and bis-p-chlorophenyl-boronic acids are incorrect.

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SYNTHESIS OF *ar*-CHLORINE-SUBSTITUTED

DICHLOROETHYLPHENYLSILANES

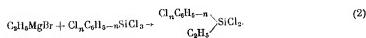
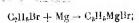
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When trichlorophenylsilane is treated with ethylin magnesium bromide, a halogen is readily replaced by an ethyl group with formation of dichloroethylphenylsilane [1]. The reaction between ethylin magnesium bromide and *ar*-chlorine-substituted trichlorophenylsilanes of various degrees of substitution has not been studied. The replacement of chlorine attached to silicon by ethyl in *ar*-chlorine-substituted trichlorophenylsilanes is of definite practical and theoretical interest. When *ar*-chlorine-substituted trichlorophenylsilanes of various degrees of substitution are used in place of trichlorophenylsilane in the reaction with ethylin magnesium bromide, the possibility will arise of the replacement by ethyl not only of chlorine attached to silicon, but also of chlorine present in the aromatic radical. In this paper we give results of a study of the reaction between ethylin magnesium bromide and *ar*-chlorine-substituted trichlorophenylsilanes.

TABLE I

Name of substance	Formula	B.p. in °C (ρ in mm.)	n_D^{20}		MR	
			found	calculated	found	calculated
Dichloro(p-chlorophenyl)ethyilsilane	$\text{Cl}_2\text{C}_6\text{H}_4\text{SiCl}_2\text{CH}_3$	116–118 (7)	1.2947	1.2720	55.06	54.79
Dichloro(2,4-dichlorophenyl)ethyilsilane	$\text{Cl}_2\text{C}_6\text{H}_3\text{Cl}_2\text{SiCl}_2\text{CH}_3$	130–132 (10)	1.4381	1.5450	58.35	59.23
Dichloro(2,4,6-trichlorophenyl)ethyilsilane	$\text{Cl}_2\text{C}_6\text{H}_1\text{Cl}_3\text{SiCl}_2\text{CH}_3$	142–144 (12)	1.4921	1.5481	64.08	64.07
Dichloroethyl(2,3,4,6-tetrachlorophenyl)silane	$\text{Cl}_4\text{C}_6\text{H}_1\text{SiCl}_2\text{CH}_3$	123–125 (3)	1.5398	1.5618	72.18	69.21
Dichloroethyl(2,3,4,6-penta chlorophenyl)silane	$\text{Cl}_5\text{C}_6\text{H}_1\text{SiCl}_2\text{CH}_3$	165–147 (3)	1.5908	1.6550	78.82	74.07

Reaction between ethylin magnesium bromide and *ar*-chlorine-substituted trichlorophenylsilanes was carried out with compounds having different degrees of substitution, namely: trichloro(p-chlorophenyl)silane, trichloro(2,4-dichlorophenyl)silane, trichloro(2,4,6-trichlorophenyl)silane, trichloro(2,3,4,6-tetrachlorophenyl)silane, and trichloro(2,3,4,5,6-penta chlorophenyl)silane. The experiments showed that ethylin magnesium bromide does not react with chlorines in the aromatic nucleus. When *ar*-chlorine-substituted trichlorophenylsilanes react with ethylin magnesium bromide under the conditions described above, the chlorine on the silicon atom is replaced by ethyl in accordance with the following scheme:



The replacement of halogen by ethyl occurred most readily in trichloro(p-chlorophenyl) silane, dichloro-(p-chlorophenyl) ethylsilane being obtained in about 70% yield. Ethylmagnesium bromide reacted with tri-chloro(2,4-dichlorophenyl) silane with formation of dichloro(2,4-dichlorophenyl) ethylsilane in 53% yield. Trichloro(2,4,6-trichlorophenyl) silane gave dichloroethyl(2,4,6-trichlorophenyl) silane in 41% yield. Trichloro-(tert- and penta-chlorophenyl) silanes exchange the chlorine attached to silicon for ethyl much less readily than the mono-, di-, and tri-chlorophenyl compounds.

As a result of the above-described reaction, some new ar-chlorine-substituted dichloroethylphenylsilanes were prepared. Some of their physical properties are given in the table.

EXPERIMENTAL

The ar-chlorine-substituted trichlorophenylsilanes used in the synthesis of ar-chlorine-substituted dichloroethylphenylsilanes were prepared by the chlorination of trichlorophenylsilane, the following procedure being adopted. A mixture of 211 g (1 mole) of trichlorophenylsilane and 1.05 g (0.5% on the weight of the silicon compound) of anhydrous ferric chloride was prepared in a three-necked flask fitted with thermometer, stirrer, and reflux condenser. The mixture was heated to 60°, and chlorine was then passed into the flask at a rate of 0.1 liter per minute. The course of the chlorination was checked by determining the change in density. During the process the temperature was maintained at 70-80°. Chlorination continued for 10-15 hours. Vacuum fractionation of the reaction product gave trichloro(p-chlorophenyl) silane, b.p. 90-95° (10 mm), d_{40}^{20} 1.4102; trichloro(2,4-dichlorophenyl) silane, b.p. 105-110° (10 mm), d_{40}^{20} 1.4801; and trichloro(2,4,6-trichlorophenyl) silane, b.p. 123-125° (10 mm), d_{40}^{20} 1.5530.

As the result of still further chlorination we isolated trichloro(2,3,4,6-tetrachlorophenyl) silane, b.p. 135-137° (10 mm), d_{40}^{20} 1.6210, and trichloro(2,3,4,5,6-pentachlorophenyl) silane, b.p. 147-150° (10 mm).

1. Preparation of Dichloro(p-chlorophenyl) ethylsilane. Magnesium turnings (24 g, i.e., 1 mole) were warmed to 36-38° in a three-necked flask fitted with thermometer, stirrer, dropping funnel, and reflux condenser, and 20 g of a mixture of ethyl bromide and ether was dropped in. Reaction soon set in. A mixture of 246 g (1 mole) of trichloro(p-chlorophenyl) silane, 110 g (1 mole) of ethyl bromide, and 100 g of toluene was then added gradually from the funnel, the reaction mixture being stirred vigorously throughout the addition. The reaction temperature was maintained at 38-40°, this being effected by control of the rate at which the addition was made and by periodic cooling of the reaction flask. When the addition was complete, the reaction mixture was heated at 70-80° for two hours with vigorous stirring. The mixture was cooled and was then filtered directly into a distilling flask fitted with a Vigreux column. The precipitate was washed with toluene (weight 135 g). The liquid phase of the reaction product was fractionally distilled: first toluene came over, and then the dichloro(p-chlorophenyl) ethylsilane fraction was separated at reduced pressure, b.p. 116-118° (7 mm), d_{40}^{20} 1.5270, and d_{40}^{20} 1.2947. The yield was 168 g (70.3%).

Found %: C 59.51; 38.80; H 3.73; 3.63; Si 10.65; 10.41; Cl 44.8; 44.4
 $\text{C}_2\text{H}_5\text{SiCl}_3$. Calculated %: C 40.14; H 3.76; Si 11.72; Cl 44.4

2. Preparation of Dichloro(2,4-dichlorophenyl) ethylsilane. The reaction conditions were the same as those used in the preparation of dichloro(p-chlorophenyl) ethylsilane. Magnesium turnings (12 g, i.e., 0.5 mole) were warmed to 36-38° in the reaction flask and 20 g of a mixture of ethyl bromide and ether was added. A mixture of 140.2 g (0.5 mole) of trichloro(2,4-dichlorophenyl) silane, 55 g (0.5 mole) of ethyl bromide, and 100 g of toluene was then added from the funnel. When the addition was complete,

reaction mixture was stirred for two hours at 70-80°, and was then cooled, filtered, and fractionated. The product isolated, amounting to 72.5 g (53.7%), was dichloro(2,4-dichlorophenyl) ethylsilane, b.p. 130-132° (10 mm), d_{40}^{20} 1.5450, and d_{40}^{20} 1.4381.

Found %: C 35.86; 35.96; H 2.95; 2.93; Si 9.70; 9.59; Cl 51.9; 51.7
 $\text{C}_2\text{H}_5\text{SiCl}_4$. Calculated %: C 35.06; H 2.92; Si 10.22; Cl 51.6

3. Preparation of Dichloroethyl(2,4,6-trichlorophenyl) silane. The reaction conditions were the same as those used in the preceding experiments. Magnesium turnings (12 g, i.e., 0.5 mole) were warmed to 36-38° in the reaction flask and 20 g of a mixture of ethyl bromide and ether was added. A mixture of 157.3 g (0.5 mole) of trichloro(2,4,6-trichlorophenyl) silane, 55 g (0.5 mole) of ethyl bromide, and 100 g of toluene was then added. When the addition was complete, the mixture was heated for two hours at 70-80° with vigorous stirring, cooled, filtered, and fractionated. The product, amounting to 63.2 g (41%), was dichloroethyl(2,4,6-trichlorophenyl) silane, b.p. 142-144° (12 mm), d_{40}^{20} 1.5491, and d_{40}^{20} 1.4925.

Found %: C 31.1; 31.5; H 2.72; 2.63; Si 9.63; 9.43; Cl 56.9; 57.0
 $\text{C}_2\text{H}_5\text{SiCl}_5$. Calculated %: C 31.14; H 2.27; Si 9.07; Cl 57.5.

4. Preparation of Dichloroethyl(2,3,4,6-tetrachlorophenyl) silane. The reaction conditions were the same as those used in the preceding experiments. Magnesium turnings (12 g, i.e., 0.5 mole) were placed in the flask, 20 g of a mixture of ethyl bromide and ether was added, and then a mixture of 175 g (0.5 mole) trichloro(2,3,4,6-tetrachlorophenyl) silane, 55 g (0.5 mole) ethyl bromide, and 100 g of toluene was added. When addition was complete, mixture was heated for 2 hours, cooled, and filtered. Toluene was distilled off, and the residue fractionated. The product, 51.4 g (30%), was dichloroethyl(2,3,4,6-tetrachlorophenyl) silane, b.p. 123-125° (3 mm), d_{40}^{20} 1.5618, and d_{40}^{20} 1.5396.

Found %: C 26.96; 27.03; H 2.22; 2.16; Si 8.33; 8.09; Cl 61.72; 61.82
 $\text{C}_2\text{H}_5\text{SiCl}_6$. Calculated %: C 28.01; H 1.95; Si 8.17; Cl 62.0

5. Preparation of Dichloroethyl(2,3,4,5,6-pentachlorophenyl) silane. The reaction conditions were similar to those used in the preceding experiments. Magnesium turnings (2 g, i.e., 0.08 mole) were warmed to 36-38° in the reaction flask, and 20 g of a mixture of ethyl bromide and ether was then added. After this "starter", a mixture of 30 g (0.08 mole) of trichloro(2,3,4,5,6-pentachlorophenyl) silane, 16 g (0.08 mole) of ethyl bromide, and 30 g of toluene was added. When the addition was complete, the reaction mixture was stirred at 70-80° for two hours, cooled, and filtered. Toluene was distilled off, and the residue was fractionated. The product, amounting to 7 g (23%), was dichloroethyl(2,3,4,5,6-pentachlorophenyl) silane, b.p. 145-147° (3 mm), d_{40}^{20} 1.5650, and d_{40}^{20} 1.5995.

Found %: C 27.38; 27.35; H 2.16; 2.35; Si 7.47; 7.74; Cl 63.26; 63.62
 $\text{C}_2\text{H}_5\text{SiCl}_7$. Calculated %: C 25.45; H 1.32; Si 7.42; Cl 65.79

SUMMARY

1. The reaction between ethylmagnesium bromide and ar-chlorine-substituted trichlorophenylsilanes was studied.
2. The following new compounds were prepared: dichloro(p-chlorophenyl) ethylsilane, dichloro(2,4-dichlorophenyl) ethylsilane, dichloroethyl(2,4,6-trichlorophenyl) silane, dichloroethyl(2,3,4,6-tetrachlorophenyl) silane, and dichloroethyl(2,3,4,5,6-pentachlorophenyl) silane.

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WURTZ SYNTHESIS OF ORGANOSILICON COMPOUNDS HAVING
A DOUBLE BOND IN THE α -POSITION

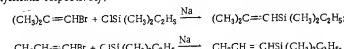
A. D. Petrov, V. F. Mironov, and V. G. Glukhovtsev

Sodium has been applied successfully in the synthesis of aromatic and aliphatic-aromatic silanes from SiCl_4 or $\text{R}_2\text{SiCl}_{4-n}$ and ArX_2 [1], but the applicability of this reaction to the synthesis of aliphatic silanes was found to be limited owing to the fact that low yields were often obtained. For example, tetraethylsilane is found in low yield by this reaction, and tetraallylsilane is not formed at all [2].

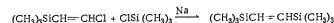
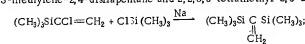
Until recently, vinyl halides and their derivatives have not been applied in the Wurtz reaction. The preparation of organosilicon compounds having a double bond in the α -position with respect to silicon has been effected by direct synthesis [3], by elimination of HCl from chlorinated organosilicon compounds [3-6] by addition of HSiCl_3 to acetylenic hydrocarbons [6], and in other ways.

These compounds were not synthesized by the organometallic method because, with the exception of β -bromotyrene, vinyl halides and their derivatives could not be converted sufficiently simply and in good yield into Mg, Li , or Na derivatives. Only recently was it found that 2-methylpropenyl bromide [7] and isopropenyl bromide [8] form organolithium compounds of adequate stability, and these were applied by Petrov and Nikishin [8] in the synthesis of a series of 1-alkenylsilanes.

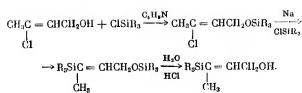
Finally, in 1953 Kanazashi [9] condensed various chloroalkylsilanes with vinyl chloride with the aid of sodium activated by ethyl acetate. He prepared dimethylvinylsilane and a series of trialkyl(α-aryl)vinylsilanes. In the present investigation we found that Kanazashi's procedure is general for the condensation of chlorosilanes not only with vinyl chloride, but also with its derivatives, i.e., compounds having the grouping $>\text{C}=\text{CH}_2$. It must be pointed out that our attempts to carry out the reaction with compounds of the type of allyl and 2-propenyl chlorides were not successful. Condensation of vinyl chloride with SiCl_4 , even with the latter in excess, gave only one product, tetravinylsilane; chlorovinylsilanes could be isolated. From 2-methylpropenyl and propenyl bromides we synthesized ethylidimethyl(2-methylpropenyl)silane and ethylidimethylpropenylsilane respectively:



The preparation of compounds of this type by the Wurtz reaction is simpler than the organolithium synthesis and does not require excess of the alkene bromide [8]. By reaction of (1-chlorovinyl)- and (2-chlorovinyl)-trimethylsilanes with $(\text{CH}_3)_2\text{SiCl}$, good yields were obtained of 1,1- and 1,2-bis(trimethylsilyl)ethylenes, i.e., 2,2,4,4-tetramethyl-1,3-methylene-2,4-disilapentane and 2,2,5,5-tetramethyl-2,5-disilahex-3-ene;



Finally, from 3-chloro-3-methylallyl alcohol (3-chloro-2-butene-1-ol), which is readily prepared from 1,3-dichloro-2-butene, 3-(trialkylsilyl)-2-butene-1-ols were prepared by the reactions given below ($\text{R} = \text{CH}_3$ and C_2H_5):



These first unsaturated organosilicon alcohols are readily cyanomethylated with acrylonitrile. The fact that, under the conditions of the Wurtz synthesis, tetravinylsilane is obtained in 65% yield, whereas tetraallylsilane is not obtained at all, is not difficult to understand in view of Petrov and Shekholovskaya's recent observation [10] that phenyllithium breaks the Si—C link in allylphenylsilane. It is evident that allylsodium formed under the conditions of the Wurtz synthesis, also breaks the Si—C link in tetravinylsilane.

TABLE

No.	Formula of compound	B.p. in °C (p in mm)	MR				Yield (%)
			η_{D}^{20}	δ_0^{a}	found	cal- cu- lated	
1	ClSi(CH ₃) ₂ Cl	151.7 (75)	1.4652	1.4232	38.45	46.64	43
	ClSi(CH ₃) ₂ CHCl	156.5 (75)	1.4551	1.3911	35.56	43.38	—
3	ClSi(CH ₃) ₂ Cl	180.9 (75)	1.4850	1.5150	43.93	44.45	44
4*	ClSi(CS) ₂ Cl	224 (74)	1.4972	1.5262	60.90	61.01	—
5	CH ₃	133 (73)	1.4745	1.4964	38.37	38.17	60
6	ClSi(CH ₃) = CHCl	124 (740)	1.4648	1.2424	38.01	38.17	—
7*	ClSi(CS) ₂ Cl ₂	198–200 (740)	1.4936	—	—	—	—
	CH ₃	—	—	—	—	—	—
8*	(CH ₃) ₂ SiCl = CHCl	116.6 (741)	1.4580	0.8920	61.30	52.65	77
	(CH ₃) ₂ SiCl = CH ₂	182–184 (741)	1.4550	0.8916	62.52	51.81	—
10*	CH ₃ Si(CH ₃) = CHSi(CH ₃) ₃	145.0 (746)	1.4310	1.5788	57.57	59.38	89.5
	CH ₃ Si(CH ₃) ₂ Si(CH ₃) ₂	151.6 (746)	1.4374	0.7824	57.75	57.97	—
12*	Si(CH ₃) = CH ₂	130.2 (746.1)	1.4625	0.7999	46.87	46.92	65
13*	CH ₃ (CH ₂) ₂ SiCH = CHCH ₃	118.5 (739)	1.4265	1.5746	63.45	58.58	52
14*	CH ₃ (CH ₂) ₂ SiCH = CHCH ₃	114.5 (743)	1.4265	1.5746	63.45	58.58	52
16*	CH ₃ (CH ₂) ₂ SiOCH ₂ CH = CS(CH ₃) ₂	116 (759)	1.4505	0.9463	48.18	49.00	52
17*	(CH ₃) ₂ SiC = CHCH ₂ CH ₃	47 (2)	1.4590	0.8694	55.22	57.98	60
	CH ₃	—	—	—	—	—	—
18*	(C ₆ H ₅) ₂ SiC = CHCH ₂ OCH ₂ CH ₃ CN	113 (2)	1.4732	0.9215	72.90	72.71	85
	CH ₃	—	—	—	—	—	—
19*	(C ₆ H ₅) ₂ SiOCH ₂ CH = CCl ₂ CH ₃	72 (2)	1.4538	0.8530	62.50	62.83	82.5
20*	(C ₆ H ₅) ₂ SiOCH ₂ CH = CS(C ₆ H ₅) ₂	104 (2)	1.4028	0.8169	54.98	55.04	52
21*	(C ₆ H ₅) ₂ SiC = CHCH ₂ OH	81 (2)	1.4725	0.8860	58.77	58.78	59
	CH ₃	—	—	—	—	—	—
22*	(CH ₃) ₂ SiC = CHCH ₂ CH ₂ OCH ₂ CH ₃ CN	65 (6)	1.4610	0.9153	59.15	59.24	80
	CH ₃	—	—	—	—	—	—

* Prepared for the first time.

The synthesis of tetraallylsilane has enabled us to establish that, unlike allyl [11], vinyl attached to silicon does not show exaltation of molecular refraction. A comparison of the Raman spectra of tetravinylsilane and triethylvinylsilane enabled the most characteristic frequencies of vinyl attached to silicon to be determined: 1272, 1404, 1594, and 3054 cm⁻¹. It was found also that the intensities of these lines increase in proportion to the number of vinyl groups, i.e., for $(\text{CH}_2=\text{CH})_n\text{Si}$ they are four times as intense as for $(\text{C}_2\text{H}_5)_3\text{SiCH}=\text{CH}_2$. Similar behavior was observed previously for allylsilanes [11]. It is interesting also to note that tetravinylsilane combines more slowly than $(\text{C}_2\text{H}_5)_3\text{SiCH}=\text{CH}_2$ with thiocyanogen.

The table gives the properties both of compounds prepared previously but now characterized in greater detail and also of compounds now synthesized for the first time.

EXPERIMENTAL

Tetravinylsilane ($\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)_3$) (1). Sodium (140 g) was melted under 500 ml of toluene in a one-liter flask fitted with reflux condenser, dropping funnel, tube reaching to the bottom for the passage of gas, and stirrer. The sodium was converted into the state of dust by rapid rotation of the stirrer. The toluene was cooled and decanted from the sodium, and 300 ml of ether and 250 g of SiCl_4 were introduced into the flask. Ethyl acetate (8-9 ml) was then added, and vinyl chloride (dried with phosphorous oxide) was passed through the stirred mixture so that the ether boiled gently. After seven hours, the precipitate was filtered off, ether was distilled from the filtrate, and the residue was vacuum-distilled (b.p., 66-68° at 90 mm). Redistillation through a column gave 70 g of (1), b.p., 120-130°, in 65% yield.

Found %: C 70.49; 70.71; H 8.91; 8.92; Si 20.82; 20.71
 $\text{C}_4\text{H}_2\text{Si}$. Calculated %: C 70.52; H 8.88; Si 20.60

$\Delta\nu$: 305 (20b), 243 (15), 584 (55), 734 (5), 962 (12), 1010 (12b), 1271 (20), 1404 (150), 1594 (160), 2846 (15), 2950 (35), 2474 (225), 3009 (20), 3054 (125).

Chlorination of $\text{C}_6\text{H}_5\text{SiCl}_3$, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{SiCl}_3$ (I), $\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{SiCl}_3$ (II), and $\text{C}_6\text{H}_5\text{SiCH}_3\text{Cl}_2$. Chlorination was carried out under ultraviolet irradiation under the conditions described previously [12]. It appeared to proceed in the liquid phase since liquid-drop condensation of the substance being chlorinated occurred in the reaction zone. In the chlorination of 2 kg of $\text{C}_6\text{H}_5\text{SiCl}_3$, a 93% yield was obtained of the compounds (I) and (II) in the proportions 1 : 1.0, in a 1 kg of $\text{C}_6\text{H}_5\text{SiCl}_3$ (II) at a temperature in the flask of up to 152°, an 89% yield was obtained of trichloro-(1,1-dichloroethyl)ilane (IV) and trichloro-(1,2-dichloroethyl)ilane (V) in the proportions 1 : 0.6. The chlorination of (IV) at temperatures according to 17-172° gave a difficultly separable mixture of (V) and tri-

chlorination of (II) at temperatures ranging up to 174° gave a difficultly separable mixture of (V) and di-chloro(2,2-dichloroethyl)silane (VI), b.p. 170-180°, in 93% yield. The chlorination of $\text{Cl}_3\text{SiCH}_2\text{SiCl}_3$ gave a 44% yield of $\text{Cl}_2\text{SiCClSiCl}_3$ (VII), b.p. 199-200°.

The elimination of HCl from (IV), the mixture of (V) and (VI), and (VII) was carried out by distilling them with quinoline [5] or with diethyl- or dimethyl-aniline and then redistilling the distillate through a column. It is more convenient to use diethyl- or dimethyl-aniline rather than quinoline, since these compounds do not form volatile salts that cause breakages in the apparatus and do not give solid residues that are difficult to remove from the flask. The mixture of (V) and (VI) gave a 60% yield of $\text{C}_8\text{H}_7\text{NICH}_2$ (CHCl (VII).

(1-Chlorovinyl) trimethylsilane [5] $\text{CH}_2 = \text{ClCSi}(\text{CH}_3)_3$ (IX). The compound (IX) (100 g) was added over a period of an hour to CH_2MgI prepared from 45 g of Mg and 350 g of CH_2I in 500 ml

The spectra were determined and interpreted by Yu. R. Egorov.

of ether. The mixture was boiled for five hours, and on the next day it was decomposed with water. Ether was removed from the ether layer, and distillation of the residue through a column gave 42 g (61.5%) of the compound (X), b.p. 104°. Color due to the presence of iodine was removed by means of aqueous sodium sulfide solution.

(2-Chlorovinyl) trimethylsilane $\text{C}_1\text{H}_3 = \text{CHSi}(\text{CH}_3)_3$ (XI). The compound (VIII) (46 g) was added over a period of two hours to CH_2MgI prepared from 18.5 g of Mg and 140 g of CH_2I in 500 ml of ether. The mixture was boiled for five hours, and the usual treatment and distillation through a column gave 25 g (77%) of the compound (XI), b.p. 114-116°.

Found %: C 44.73; 44.6; H 8.33; 8.30; Si 20.65; 20.45; Cl 26.80; 25.70
 $\text{C}_8\text{H}_{11}\text{SiCl}$. Calculated %: C 44.59; H 8.31; Si 20.83; Cl 26.83

(1-Chlorovinyl) triethylsilane $\text{CH}_2 = \text{CICSi}(\text{CH}_3)_3$ (XII). The compound (IX) (18.9 g) was added to $\text{C}_8\text{H}_8\text{MgBr}$ prepared from 77 g of Mg and 420 g of $\text{C}_8\text{H}_8\text{Br}$ in 1500 ml of ether. On the next day, after a two-hour boil and the usual treatment, 133 g (78.5%) of the substance (XII), b.p. 183°, was obtained.

Found %: C 54.06; 54.10; H 9.63; 9.64; Si 16.14; 15.97
 $\text{C}_8\text{H}_{11}\text{SiCl}$. Calculated %: C 54.36; H 9.69; Si 15.87

2,2,4,4-Tetramethyl-2-methylene-2,4-disilapentane [$(\text{CH}_3)_2\text{Si}_2\text{C} = \text{CH}_2$] (XIII). Sodium (9 g) was melted under 30 ml of toluene and converted by stirring into fine dust. The mixture was cooled, and 500 ml of ether, 20 g of $(\text{CH}_3)_2\text{SiCl}$, 1.2 ml of (X), and 1.2 ml of ethyl acetate were added. When reaction had set in, 23.5 g of (X) was added at such a rate that the ether boiled gently. The mixture was then heated for 2.5 hours. The precipitate was filtered off, ether was distilled from the filtrate, and the residue was distilled through a column and gave 14 g (46.5%) of (XIII), b.p. 151°.

Found %: C 55.97; 55.99; H 11.50; 11.58; Si 32.55; 32.57
 $\text{C}_8\text{H}_{12}\text{Si}_2$. Calculated %: C 55.74; H 11.69; Si 32.65

2,2,5,5-Tetramethyl-2,5-disilahept-3-ene ($\text{CH}_3)_2\text{SiCH} = \text{CHSi}(\text{CH}_3)_3$ (XIV). Sodium (10 g) was granulated in isooctane, 250 ml of ether was added, and to the suspension so obtained 25 g of $(\text{CH}_3)_2\text{SiCl}$ and 2 ml of (X) were added. Reaction was initiated by addition of 0.1-2 ml of ethyl acetate, and 27 g of (X) was then added. The mixture was boiled for four hours, and the precipitate formed was filtered off. The product, amounting to 34 g (76%), was the compound (XIV).

Found %: C 56.06; 55.99; H 11.82; 11.69; Si 32.59; 32.35
 $\text{C}_8\text{H}_{12}\text{Si}_2$. Calculated %: C 55.74; H 11.69; Si 32.65

Ethyldimethyl(2-methylpropenyl)silane $\text{C}_8\text{H}_9(\text{CH}_3)_2\text{SiCH} = \text{C}(\text{CH}_3)_2$ (XV). To 17 g of sodium in 250 ml of ether, 41 g of $\text{C}_8\text{H}_9(\text{CH}_3)_2\text{SiCl}$ and 1 ml of ethyl acetate were added. 2-Methylpropenyl bromide (47 g) was then added gradually. The usual treatment gave 23.8 g (50.1%) of (XV).

Found %: C 67.74; 67.56; H 12.75; 12.58; Si 19.71; 19.54
 $\text{C}_8\text{H}_{10}\text{Si}$. Calculated %: C 67.52; H 12.75; Si 19.72

Ethyldimethylpropenylsilane $\text{C}_8\text{H}_9(\text{CH}_3)_2\text{SiCH} = \text{CHCH}_2$ (XVI). To 17 g of sodium in 250 ml of ether, 43 g of $\text{C}_8\text{H}_9(\text{CH}_3)_2\text{SiCl}$ and 1 ml of ethyl acetate were added. Propenyl bromide (47 g) was added in portions. The usual treatment gave 14 g (32.5%) of (XVI), b.p. 114.5-119.5°.

Found %: C 65.72; 65.70; H 12.30; 12.28; Si 22.37; 22.04
 $\text{C}_8\text{H}_{10}\text{Si}$. Calculated %: C 65.54; H 12.57; Si 21.87

(3-Chloro-2-butenyloxy) trimethylsilane $\text{CH}_2\text{C} = \text{CHCH}_2\text{OSi}(\text{CH}_3)_3$ (XVII).

A mixture of 52 g of $(\text{CH}_3)_2\text{SiCl}$ and 39 g of 3-chloro-2-buten-1-ol was boiled for four hours until HCl ceased to separate. Distillation through a column gave 33 g (50.8%) of (XVII), b.p. 162-165°.

Found %: C 46.54; 46.69; H 8.08; 8.29
 $\text{C}_8\text{H}_{10}\text{SiOCl}$. Calculated %: C 47.00; H 8.48

(3-Chloro-2-butenyloxy) triethylsilane $\text{CH}_2\text{C} = \text{CHCH}_2\text{OSi}(\text{CH}_3)_3$ (XVIII).

C1
3-Chloro-2-buten-1-ol (100 g) was added to a stirred mixture of 142 g of $(\text{CH}_3)_2\text{SiCl}$, 80 g of pyridine, and 250 ml of benzene. After two days the precipitate of pyridine hydrochloride was filtered off. Fractionation of the filtrate gave 142 g (82.5%) of (XVIII), b.p. 70-72° (2 mm).

Found %: C 63.80; 53.85; H 9.38; 9.36; Cl 16.33; 16.02; Si 12.09; 11.55
 $\text{C}_8\text{H}_{10}\text{SiOCl}$. Calculated %: C 54.39; H 9.59; Cl 16.06; Si 12.70

2,2,6,7,7-Pentamethyl-3-oxa-2,7-disilaoct-5-ene

$(\text{CH}_3)_2\text{SiC} = \text{CHCH}_2\text{OSi}(\text{CH}_3)_3$ (XIX).

Reaction was initiated in a mixture of 8 g of sodium, 200 ml of ether, and 21 g of $(\text{CH}_3)_2\text{SiCl}$ by addition of ethyl acetate, and 28.5 g of (XVII) was then added over a period of two hours. A three-hour boil followed by the usual treatment gave 18 g (52%) of (XIX), b.p. 195°.

Found %: C 55.35; 55.42; H 10.97; 11.14; Si 25.77; 25.68
 $\text{C}_8\text{H}_{12}\text{Si}_2\text{O}$. Calculated %: C 55.86; H 11.11; Si 25.93

3,3,8,8-Tetraethyl-7-methyl-4-oxa-3,8-disiladex-6-ene

$(\text{CH}_3)_2\text{SiC} = \text{CHCH}_2\text{OSi}(\text{CH}_3)_3$ (XX).

C_8H_{12}
To a mixture of 25.5 g of sodium, 500 ml of ether, and 85 g of $(\text{CH}_3)_2\text{SiCl}$, 120 g of (XVII) was added. The precipitate was filtered off on the next day, and distillation gave 85 g (52%) of (XX), b.p. 101° (2 mm).

Found %: C 62.95; 62.90; H 11.98; 12.12; Si 18.15; 18.39
 $\text{C}_8\text{H}_{12}\text{Si}_2\text{O}$. Calculated %: C 63.94; H 12.04; Si 18.07

3-(Trimethylsilyl)-2-buten-1-ol ($\text{CH}_3)_2\text{SiC} = \text{CHCH}_2\text{OH}$ (XXI).

C_8H_{12}
A mixture of 16 g of (XIX), 20 ml of ethanol, 30 ml of water, and four drops of hydrochloric acid was boiled for eight hours. The product was dried with sodium sulfate and fractionated, when 5 g (60%) of (XXI), b.p. 46-47° (2 mm), was obtained.

Found %: C 58.24; 58.28; H 11.27; 11.11; Si 19.66; 19.54
 $\text{C}_8\text{H}_{10}\text{SiO}$. Calculated %: C 58.30; H 11.19; Si 19.42

3-(Triethylsilyl)-2-buten-1-ol ($\text{CH}_3)_2\text{SiC} = \text{CHCH}_2\text{OH}$ (XXII).

C_8H_{12}
A mixture of 77 g of (XX), 100 ml of ethanol, 23 ml of water, and 3 ml of hydrochloric acid was boiled for three hours. On the next day the mixture was dried and fractionated, when 25 g (59%) of (XXII), b.p. 81° (2 mm), was obtained.

Found %: C 63.58; 63.68; H 11.88; 12.01; Si 15.78; 15.73
 $\text{C}_8\text{H}_{10}\text{SiO}$. Calculated %: C 64.45; H 11.91; Si 15.05

In presence of sodium methoxide, (XXII) combined with acrylonitrile with evolution of heat. The addition product was obtained in 85% yield.

Found %: C 65.44; 65.33; H 10.69; 10.54; Si 11.69; 11.41
 $\text{C}_8\text{H}_{10}\text{SiOH}$. Calculated %: C 65.21; H 10.52; Si 11.72

SUMMARY

1. It was shown that organosilicon compounds having a double bond in the α -position with respect to silicon can be synthesized in high yield by the condensation of chlorotrialkylsilanes with vinyl halide derivatives in ether in presence of sodium activated by ethyl acetate.

2. Silicon tetrachloride was condensed with $\text{CH}_2 = \text{CHCl}$, and R_3SiCl was condensed with $\text{CH}_2 = \text{CHCl}$,

R_2SiCl was condensed with $\text{CH}_2\text{CH}=\text{CHBr}$, $(\text{CH}_3)_2\text{C}=\text{CHBr}$, $(\text{CH}_3)_2\text{SiCH}=\text{CHCl}$, $(\text{CH}_3)_2\text{SiCCl}-\text{CH}_2$, and $\text{R}_2\text{SiOCH}_2\text{CH}=\text{CCl}$ ($\text{R} = \text{CH}_3$ and C_2H_5).

3. Sixteen organosilicon compounds were prepared for the first time. These included tetravinylsilane and 3-(trialkylsilyl)-2-butene-1-ols.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 14. INTERCONVERSION OF 1- AND 2-BUTENES

UNDER THE CONDITIONS OF CATALYTIC HYDROCONDENSATION

OF CARBON MONOXIDE WITH OLEFINS

Ya. T. Eidus and R. I. Izmailov

Apart from deuteropropene, the normal butenes are the simplest olefins capable of undergoing isomerization by displacement of the double bond (interconversion of 1- and 2-butene). These transformations can occur at the actual moment when the butene is formed, e.g., in the dehydration of butanols, the dehydrogenation of butane, the dimerization of ethylene, and other such processes, and also when it is formed intermediate in other reactions.

The interconversion of 1- and 2-butene is not only of theoretical, but also of practical interest, since in any process one of the isomers may be preferable to the other as starting material [1]. The purely thermal isomerization of the butenes by double-bond displacement occurs at comparatively high temperatures - of the order of 600-650° [2]. A claim made in a patent [3], according to which 1-butene undergoes 87% conversion into 2-butene at 55° in an empty quartz tube, is not very probable since the content of 1-butene in the equilibrium mixture of butenes at this temperature is not more than 35% [4]. At lower temperatures displacement of the double bond can occur only in presence of catalysts. No isomerization of 2-butene into 1-butene was observed at 390°, although cis-trans interconversion proceeded at an appreciable rate [5]. The displacement of the double bond in butenes, occurring in the substances as such or occurring at the moment of their formation, particularly from butanols, has been investigated over various catalysts, of which the most active were found to be, on the one hand, acidic catalysts - sulfuric [6] and phosphoric [6-10] acids, as such or supported on solid carriers, phosphoric oxide [3], aluminum sulfate [7, 8, 11], aluminum phosphate [6], silica gel [7], alumina apparently when containing acidic impurities [7, 12-15], and natural and synthetic aluminosilicates [16-19] - and, on the other hand, metals and their oxides - ThO_2 [20], $\text{Co}-\text{Cu}-\text{ThO}_2$ [12], Co on charcoal [21] and metallic nickel [22, 23]. It must be pointed out that reaction over metallic nickel occurs only in the presence of hydrogen [23]. The dimerization of ethylene at 35-40° and 50 atm over cobalt deposited on charcoal yielded a mixture of 1- and 2-butenes, and the relative amount of 1-butene fell as the space velocity of the ethylene was lowered, which indicates that the 1-butene formed initially was isomerized into 2-butene. Over the catalyst $\text{Co}-\text{Cu}-\text{ThO}_2$, which is active in the synthesis of hydrocarbons from carbon monoxide and hydrogen, the treatment of 1-butene at 190° and atmospheric pressure gave a gas containing 3.8% of 2-butene [12]. When the reaction products were again passed over the catalyst, the outgoing gas already contained 55% of 2-butene. In a similar experiment with cis-2-butene, the outgoing gas contained 7% of 1-butene. In experiments lasting 20-24 hours in a circulating system, equilibrium was attained when the original gas was cis-2-butene or a mixture containing 13.8% of 1-butene. The equilibrium mixture contained 11.3% of 1-butene, 31.0% of cis-2-butene, and 57.7% of trans-2-butene; no isobutene was formed. However, over a catalyst that had not been regenerated practically no displacement of the double bond occurred.

The present investigation had the object of determining the possibility of the isomerization of 1-butene into 2-butene, and of the reverse reaction, under the conditions required for the catalytic hydrocondensation of carbon monoxide with olefins [24]. This question has a direct bearing on a previous investigation on the hydrocondensation of carbon monoxide with butene obtained by the dehydration of 1-butanol over alumina at

400° [25] and also on the view that the formation of hydrocarbon chains in the hydrocondensation of carbon monoxide with ethylene and propane proceeds stepwise, and therefore with the intermediate formation of butene. In order to resolve this question, an investigation was made of the behavior of 1- and 2-butenes over a catalyst for the reaction of hydrocondensation at atmospheric pressure and 190° in absence and in presence of hydrogen, but always in absence of carbon monoxide.

EXPERIMENTAL

The determination of the composition of the mixture of butenes was one of the most complicated tasks arising in the investigation of the isomerization of butenes. Analytical errors give rise to numerous discrepancies between the results obtained by different authors. Various methods based on the bromination of the mixture of butenes, which have been used previously [6, 13, 17], were found to be inaccurate owing to the possibility of the thermal isomerization of the dibromides during fractionation. Low-temperature fractionation of butenes through a Podbielniak column [6, 7, 12, 15] supplemented by the usual gas analysis of the fractions [7, 12], is also inadequate. A simple, rapid method of determining the composition of a liquid mixture of normal butenes is the measurement of its vapor pressure at -80° [22] or 0° [26].

We used a combined method for the determination of mixtures of butenes; it included low-temperature fractionation through a Podbielniak column, sulfuric acid analysis of the fractions supplemented by a test for isobutene with the Deniges reagent, and determination of the vapor pressures of the liquefied fractions at 0°. In calculating the composition of mixtures from vapor pressures we used Raoult's law. The linearity of the relationship between vapor pressure and molar composition has been shown previously [18]. The probable error in the method based on vapor pressure at 0° is less than 1%. Vapor pressures at 0° P₀ are as follows [26]: isobutene 98.4 ± 0.6 mm, 1-butene 96.4 ± 1 mm, trans-2-butene 73.65 ± 0.3 mm; cis-2-butene 66.1 ± 1.5 mm, and butane 77.5 mm [27].

Preparation of 1-Butene

Freshly prepared butyl alcohol - b.p., 116.5-117.0° (756 mm); n_D²⁰ 1.3991, d₄²⁰ 0.8098; found MR 221.3°, calculated for C₄H₉OH MR 222.20 (the literature [28, 29] gives n_D²⁰ 1.3992, d₄²⁰ 0.80978). It was dehydrated over commercial alumina at 390°. The resulting gas was dried over calcium chloride and frozen out with a mixture of solid carbon dioxide and acetone. In order to enrich it in 1-butene, the liquid butene was fractionated through a Podbielniak low-temperature column, the distillate being collected from -62° upwards. The result of such a fractionation (28 ml of liquid butene) is given in Table 1.

TABLE I

Fraction	Boiling limits (°C)		Yield of fraction (liters of gas)	Vapor pressure at 0° P ₀ (mm)	1-Butene content (%)	2-Butene content (%)
	From -6.2 to -5° (inclusive)	From -5 to 0.8				
I	From -6.2 to -5° (inclusive)	5.4	952	96.5	4.5
II	From -5 to 0.8	1.0	860	55.5	44.5
III	From -5 to 0.8	to +3	0.65	782	21.8	78.7

Refractionation of Fraction I through the same column gave a narrow fraction of b.p. -5° and P₀ 962.6 mm, which corresponds to 94.4% of 1-butene and 5.6% of 2-butene; it comprised about 69% of Fraction I and about 45% of the original butene. In other batches treated in this way we succeeded in obtaining 1-butene having P₀ 964 mm.

* Fraction I contained about 0.4% of isobutene.

Preparation of 2-Butene

2-Butene was prepared from 2-butanol by dehydration over alumina at 340°. The 2-butanol was prepared by the hydrogenation of 2-butanone, and it was distilled through a 40-plate column before use; it had b.p. 99.5° (758 mm), d₄²⁰ 1.3970, d₄²⁰ 0.8068, found MR 22.11; calculated for C₄H₈O MR 22.20 (the literature [30] gives n_D²⁰ 1.39780 [31], 1.39713 [32], d₄²⁰ 0.8063 [29], b.p. 99.5° (760 mm), [34] 99.5°). The butene so obtained contained 99% of normal butene and about 1% of isobutene; when liquefied it had P₀ 715 mm.

Liquid butene (175 ml) was fractionated through the low-temperature column, and 6 liters of gas (13,779) came over from -4° to +0.8° (0° to -4°, 2.5 liters came over; from -4° to -1°, 1.5 liters; from -1° to +0.2°, 1 liter; and from +0.2° to +0.8°, 1 liter). This fraction (b.p. from -4° to +0.8°) had P₀ 1050 mm. The whole of the residue (86.3%) was fractionated through the same column over the range 0.8-4° into five different fractions, each consisting of 30 ml of liquid, and having P₀ = 746, 743, 732.8, 729.8, and 728 mm respectively. The last fraction (P₀ = 731 mm), which contained neither 1-butene nor isobutene, was taken for the experiments.

In all of the experiments the catalysts (50 ml each) were taken from the same preparation; before use they were treated with hydrogen at 450°. Their activity in the reaction of hydrocondensation of carbon monoxide with olefins, which was tested with a gas mixture consisting of 70% C₂H₄, 5% CO, and 25% H₂ at 190° and at a space velocity of 100 hour⁻¹, may be expressed by the yield of hydrocarbons, which was about 500 ml per cu.m. After the isomerization experiments the catalysts preserved their activity for the hydrocondensation reaction. The experiments were carried out in a glass tube 12 mm in diameter,

1) In Absence of Hydrogen (Experiment 287, Catalyst 64). In order to remove hydrogen completely from the surface of the catalyst, nitrogen was displaced at 190°, and 1-butene (P₀ 964 mm) was passed for two hours at a space velocity of 70 hour⁻¹. The volume passed was 4200 ml, and 2800 ml of gas was recovered having P₀ 924 mm and a composition of 98.6% n-C₄H₈ and 1.4% C₄H₁₀, which corresponds to 83.3% of 1-butene, 15.3% of 2-butene, and 1.4% of butane*. Under the same conditions a further 2630 ml of the same 1-butene was passed, and 2600 ml of gas was recovered having P₀ 953 mm and a composition of 100% of n-butene; finally a further 2100 ml of 1-butene was passed and 2100 ml of gas was recovered having P₀ 953 mm and a composition of 100% of n-butene. Both of the last two portions of gas obtained by passage of 1-butene over the catalyst had the composition of 95.8% of 1-butene and 4.2% of 2-butene*. Thus, in absence of hydrogen 1-butene undergoes very little isomerization (about 4%); when hydrogen is present in the catalyst but not in the original gas, 1-butene isomerizes to the extent of about 15%.

2) In Presence of Hydrogen (Experiment 288, Catalyst 65). A gaseous mixture consisting of 90.1% of 1-butene (P₀ 962.5 mm, corresponding to 0.6% of 2-butene) and 9.9% of hydrogen was passed at 190° over Catalyst 65 at a space velocity of 66 hour⁻¹. The volume passed was 7700 ml, including 6900 ml of butene and 760 ml of hydrogen. The outgoing gas was frozen out at -7°, 225 ml of gas not being condensed at this temperature (8.2% C₂H₄, 91.8% H₂ + CH₄ + C₂H₆). About 15 ml of liquid was condensed, and on evaporation this gave 3700 ml of gas of composition 0.4% of isobutene, 90.5% C₄H₈, and 9.1% C₄H₁₀+. The condensate was fractionated through a Podbielniak column, and the part boiling below the butenes (from -103° to -30°), which comprised 4.4% of the condensate, had the composition 16.5% C₄H₁₀, 22.0% C₄H₈, and 61.5% C₄H₁₀+. (n < 4). The fractionation curve for this part of the condensate is shown in Fig. 1.

From the curve in Fig. 1 it can be calculated that C₄H₄ : C₄H₈ : C₄H₁₀ = 1.0 : 1.1 : 1.5. The second row of figures along the axis of abscissae in Fig. 1 give the percentage of the whole condensate. The remaining 95.6% of the condensate formed the C₄ fraction and had the following composition: 0.4% of isobutene, 90.9%

* Calculated for the formation of an equilibrium mixture of cis- and trans-2-butenes. When calculated for trans-2-butene, 16.2% of 2-butene is obtained instead of 15.3%.

+ Calculated for an equilibrium mixture of the two forms of 2-butene; when calculated for trans-2-butene a composition of 95.8% of 1-butene and 4.2% of 2-butene is obtained.

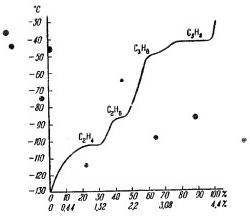


Fig. 1. Fractionation curve for products boiling below the butenes formed in the isomerization of 1-butene (Experiment 288)

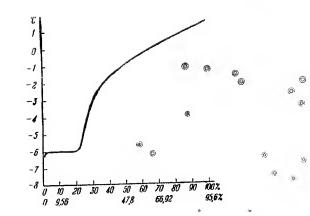


Fig. 2. Fractionation curve for the C₄ fraction of products formed in the isomerization of 1-butene (Experiment 288)

of n-butenes, and 8.7% of butane. The C₄ fraction of the reaction product was fractionated through the same column. The results of the fractionation are given in Table 2. The contents of 1- and 2-butene were calculated from the vapor pressures P_v, taking into account the contents of butane, isobutene, and n-butene found by gas analysis.

The fractionation curve for the C₄ fraction is shown in Fig. 2. No residue corresponding to C₅ hydrocarbons and hydrocarbons of still higher boiling point was obtained.

It follows from Table 2 that the C₄ fraction of the product of the isomerization of 1-butene in presence of 10% of hydrogen had the following composition: 41.9% of 1-butene, 47.5% of 2-butene, 10.4% of butane, and 0.2% of isobutene. From the data on the composition of P_v of Fraction III, which contained the bulk of the 2-butene (89%), it was found that the relative amounts of cis- and trans-2-butenes in this fraction was 1:4.3.

Hence, the isomeric transformation of 1-butene into 2-butene occurs at 190° in presence of 10% of hydrogen. At a space velocity of 66 hour⁻¹ a mixture was obtained in which the relative amounts of 1- and 2-butene were 1:1, the equilibrium ratio at 190° being 10.8:89.2 [14]. The relative amounts of cis- and trans-2-butene were 1:1, the equilibrium ratio 29.5:59.7 [4]. In the course of the reaction partial hydrogenation occurred: The C₄ fraction contained 10.4% of butane. Hydrogenolysis and skeletal isomerization of 1-butene occurred to a negligible extent.

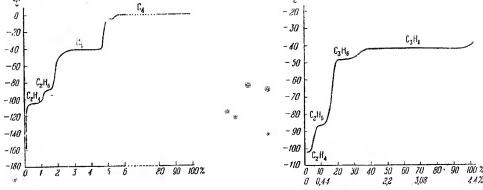


Fig. 3. Fractionation curve for products obtained in the isomerization of 2-butene (Experiment 291)

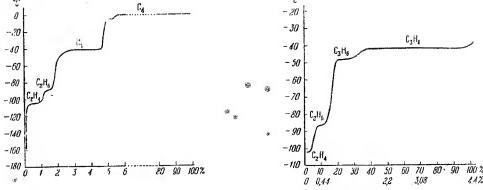


Fig. 4. Fractionation curve for products boiling below the butenes formed in the isomerization of 2-butene (Experiment 292)

Experiments on the Isomerization of 2-Butene into 1-Butene

1) **In Absence of Hydrogen** (Experiment 289, Catalyst 66). Hydrogen was displaced from the reaction tube with nitrogen at 250°, and then 2-butene was passed at 190° with the result that some hydrogenation occurred [the outgoing gas (600 ml) contained 82.7% of butene and 17.3% of butane]. More 2-butene (P_v 731 mm, 96.5% trans and 3.5% cis) was then passed over the catalyst at 190° at a space velocity of 66 hour⁻¹. The volume of gaseous 2-butene that was passed was 3500 ml, and this was recovered almost without change in volume; it contained 100% of 2-butene and after liquefaction had P_v 731.5 mm. Under these conditions, therefore, 2-butene is not isomerized into 1-butene and does not undergo cis-trans isomerization.

Experiment 290. 2-Butene (3700 ml, P_v 731 mm) was passed over the same catalyst at the same space velocity at 230°. The outgoing gas had P_v 739.5 mm after liquefaction and contained 0.7% of isobutene and 99.3% of n-butene. These results correspond to a 1-butene content of 2.9%. Hence, even at a higher temperature (230°) the extent to which double-bond displacement occurs in 2-butene is very small.

2) **In Presence of Hydrogen** (Experiment 291, Catalyst 67). A gaseous mixture (7200 ml) of 90% 2-butene (P_v 728 mm, 6.8% cis and 93.2% trans) and 10% hydrogen was passed over the catalyst at 190° and at a space velocity of 66 hour⁻¹. The volume of gas received was 3600 ml, the liquefaction of which gave 15 ml of liquid having P_v 881.5 mm and composition: 0.3% of isobutene, 93.2% C₄H₁₀, and 6.5% C₄H₁₀⁺. This 15 ml was fractionated through a Podbielinsk column with the following results: driven off up to -40°, 153 ml of gas (Fraction I), which formed 4.6% of the whole and had the composition 15.2% C₄H₆, 34.3% C₄H₈, and 49.9% C₄H₁₀⁺. The residue (P_v 729.5 mm) was fractionated into two fractions. Fraction II (23 ml of gas), b.p. from -7° to 25°, and Fraction III (3330 ml of gas), b.p. 3-5°. Fraction III did not contain isobutene and consisted of 95.5% of n-butene and 4.5% of butane. It follows from these data that the overall composition of the condensed gas was 0.75% of ethylene, 1.6% of propane, 4.2% of butane, 90.4% of 2-butene, 2.2% of ethane + propane, and 0.7% of 1-butene + isobutene.

In Experiment 291 not only gas, but also 0.3 ml of liquid condensable at room temperature was obtained, this representing a yield of liquid hydrocarbons of 37.5 ml per cu.m.

Hence, in the study of the displacement of the double bond in 2-butene in presence of 10% of hydrogen at 190°, practically no 1-butene was detected in the reaction products. Partial hydrogenation and hydrogenolysis occurred and, to a very slight extent, also hydropolymerization.

Experiment 292. An isomerization experiment was carried out with the same Catalyst 67 on a mixture of 73.4% of 2-butene (P_v 728 mm) and 26.6% of hydrogen at 190° and a space velocity of 100 hour⁻¹. The volume of gaseous mixture passed was 9000 ml, and the products were 0.5 ml of liquid condensate (50 ml per cu.m), 3750 ml of gas, which condensed to 15 ml of liquid, and 900 ml of gas, which did not condense at -70°.

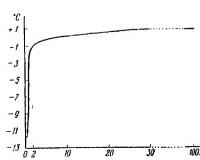


Fig. 5. Fractionation curve for the C_4 fraction from 2-butene (Experiment 292)

The condensed gas had the following composition: 0.3% C_2H_2 , 1.3% C_3H_6 , 0.6% of 1-butene (in admixture with isobutene), 88.0% of 2-butene, 2.8% of $C_2H_4 + C_3H_6$, and 7% of C_4H_{10} . It will be seen from these results that 1-butene is practically absent from the outgoing gas.

TABLE 3

Original gas	Space velocity (hour ⁻¹)	Composition of C_4 fraction of reaction product (%)			
		1-Butene	2-Butene	Butane	1-Butene
1-Butene	0	70	95.8	4.2	—
1-Butene	9.9	66	41.0	47.5	10.4
2-Butene	0	66	—	100	—
2-Butene	10	69	0.7	94.9	4.4
2-Butene	26.6	100	0.7	92.0	7.3
					1 : 171

Table 3 gives a general summary of the results obtained on the isomerization of 1-butene into 2-butene and vice versa over a hydrocondensation catalyst at 190°.

It is notable that 1-butene is isomerized into 2-butene in presence of hydrogen, a fact that proves the activity of the catalyst for this reaction. A considerable proportion of the 1-butene remains adsorbed on the catalyst surface, when the initial gas consists entirely of olefin (hydrogen absent), the extent to which it is absorbed is less. It appears that, in presence of hydrogen, 2-butene is isomerized into 1-butene, but this remains adsorbed on the catalyst surface,

SUMMARY

1. The catalytic reaction 1-butene \rightleftharpoons 2-butene was studied both in presence and in absence of hydrogen, the conditions being those for the hydrocondensation of carbon monoxide with olefins, carbon monoxide, however, being absent.

2. It was shown that, in absence of hydrogen, the isomerization of 1-butene into 2-butene and vice versa did not occur to an appreciable extent.

3. In presence of 10% of hydrogen, 1-butene was isomerized into 2-butene, the relative amounts of 1- and 2-butenes in the products being 1 : 1.1 (at a space velocity of 66 hour⁻¹).

4. In experiments on the isomerization of 2-butene in presence of 10% and 26.6% of hydrogen at space velocities of 69 and 100 hour⁻¹, no appreciable amount of 1-butene could be detected in the reaction product.

5. In experiments with 1-butene, hydrogenation of the olefin proceeded much more rapidly (about twice as fast) than in experiments with 2-butene under similar conditions.

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N. D. Zelinsky Institute of Organic
Chemistry of the Academy of Sciences
of the USSRCATALYTIC HYDROCONDENSATION OF CARBON
MONOXIDE WITH OLEFINSCOMMUNICATION 15. HYDROCONDENSATION OF CARBON
MONOXIDE WITH 2-BUTENE

Ya. T. Eidus and R. I. Izmailov

In a previous communication [1] we described experiments on the hydrocondensation of carbon monoxide with the butene obtained by dehydration of butyl alcohol over alumina, which consists of a mixture of 1- and 2-butene, the former predominating. We used an equimolecular mixture of the butene obtained in this way and hydrogen, and 4-6% of carbon monoxide was added. The hydrocondensation reaction gave liquid hydrocarbons in a yield of 63% ml per cu.m, or 55 ml per liter of catalyst per hour. About 30-35% of the olefin that reacted was hydrogenated to butane. After being "debutanized", the liquid condensate boiled over the range 28-27° and contained 28% of olefins; after hydrogenation the following fractions were found (% by volume): about 24% of the C₆ fraction (about half of this was isopentane), 15% of the C₅ fraction, 8% each of the C₄ and C₃ fractions, and 9% of the C₂ fraction.

It was of interest to investigate the behavior of 2-butene in the reaction of hydrocondensation with carbon monoxide, for there were no data on the behavior of symmetrically disubstituted ethylenes in this reaction. When an attempt was made to use cyclohexene - which can be regarded as a symmetrically disubstituted ethylene - in the reaction of hydrocondensation with carbon monoxide [2], it was found that "irreversible" catalysis and hydrogenation to cyclohexane occurred, but methylation with formation of methyl- and 1,2-dimethylcyclohexenes occurred only to a slight extent.

The object of the present investigation was the study of the hydrocondensation of carbon monoxide with 2-butene. The apparatus and experimental procedure were the same as in previous work [1]. The preparation of pure 2-butene for use as a component of the initial gas mixtures and the method of determining the composition of the C₄ fraction were described in the preceding paper [3]. All of the catalysts were samples from the same preparation.

EXPERIMENTAL

Table I gives details of experiments on the hydrocondensation of carbon monoxide with 2-butene at 180° and atmospheric pressure in a continuous-flow system. The glass reaction tube was 12 mm in diameter. Catalysts 68-72 were used (30 ml of each, except Catalyst 71, of which 50 ml was taken), and these were regenerated after every 15 hours. The ingoing mixture was prepared from 2-butene that contained no 1-butene or isobutene as impurity and had a vapor pressure at 0° (P₀) of 728-732 mm, which corresponds to trans-2-butene in admixture with 2,2-7,6% of cis-2-butene. The mixture consisted of 70-75% of 2-butene, 21-26% of hydrogen, and 4-6% of carbon monoxide.

The gas was passed over the catalyst at a space velocity of 100 hour⁻¹. As can be seen from Table I, the yield of liquid hydrocarbons calculated on C₄H₈ + H₂ + CO was 350-550 ml per cu.m or 32-55 ml per liter of catalyst per hour, the contraction in the gas being 33-39.5%. The ratio of heavy oil to light was 1.2 : 3.2.

TABLE 1

Catalyst	Experiment	Duration of exp. (hours)	Space velocity (hour ⁻¹)	Composition original gas (% by vol.)			Yield (ml/cu.m)	Yield of H + L (ml/liter-hour)			
				2-Butene	II _s	CO					
68	293	6.5	91	35.0	72.7	22.6	4.7	254.2	101.7	355.9	32.3
68	294	6.5	100	35.7	74.4	21.2	4.4	204.1	173.5	377.5	45.9
69	295	12.0	99	37.3	72.2	23.1	4.2	204.1	173.5	377.5	45.8
69	296	13.0	100	33.0	71.3	23.3	5.4	200.3	223.5	342.3	55.5
70	297	12.0	100	33.0	71.3	23.3	5.4	200.3	92.0	391.3	39.6
71	298	11.0	103	38.5	72.0	22.1	5.9	264.5	57.3	348.9	35.8
72	299	12.5	102	39.5	72.0	23.0	4.2	243.1	101.5	344.6	35.2
72	300	23.2	102	33.3	70.0	20.0	4.0	243.1	101.5	405.1	40.5
72	301	40.0	100	34.3	70.7	24.2	5.1	219.8	185.3	—	—

TABLE 2

Fraction	B.p. (°C)	Composition of fraction			Content of fraction in outgoing gas
		Gas	(% on -1)(% on outgoing fraction) going gas)		
I	-160 to -110	He	63.0	16.4	2.8
		CO	14.6	3.5	
		CH ₄	22.4	5.8	
II	-110 to -10	C ₂ H ₂	2.8	0.43	74.0
		C ₂ H ₄	1.8	0.3	
		C ₂ H ₆	3.3	0.24	
III	-10 to 2	2-Butene	95.5	66.4	4.5
		Butane	4.5	3.14	

In some experiments the composition of the outgoing gas was determined, and on the basis of the results obtained the extent to which each component of the original mixture took part in the reaction was determined. As an example we will cite the results obtained in Experiment 294 (Table 1). In this experiment we passed 18600 ml of gas (STP) of the composition shown in Table 1 and, apart from liquid condensate, we obtained 11600 ml of gas, of which 2700 ml did not condense and 8900 ml did condense at -70°. Part (3000 ml) of the gas obtained was fractionated through a Podbielniak low-temperature column. The results of the fractionation are shown in Table 1 and Fig. 1.

Fraction III had P₀ 732 mm and contained neither 1-butene nor isobutene. The original 2-butene had P₀ 731 mm, corresponding to trans-2-butene in admixture with 3.4% of cis-2-butene. Fraction III contained 4.5% of cis-2-butene. Analysis of the results given in Table 2 showed that 2-butene reacted to the extent of 47.2% hydrogen to the extent of 54.3% and carbon monoxide to the extent of 45.0%. The products of hydrocracking (C₁ + C₂ + C₃) correspond to about 2% of the original 2-butene and about 4% of the 2-butene that reacted; the corresponding figures for butane were 2.5% and 5.0% approximately.

The liquid condensate (about 170 ml) obtained in Experiments 293-301 was separated from water formed in the reaction, washed twice with 2% caustic soda, washed with water until neutral, and sealed in a tube over anhydrous copper sulfate. After being dehydrated, the condensate was filtered from copper sulfate and "debutanized" in a low-temperature column, about 18% by volume of the condensate being distilled off below 20°, the

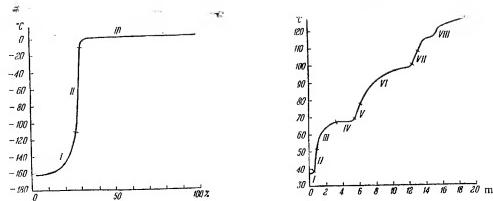


Fig. 1. Fractionation curve for the gaseous fraction of the products of the hydrocondensation of carbon monoxide with 2-butene

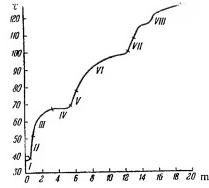


Fig. 2. Fractionation curve for liquid hydrocarbons obtained in the hydrocondensation of carbon monoxide with 2-butene

TABLE 3

Fraction	B.p. (°C)	Content of fraction in original condensate	n _D ²⁰	d _A ²⁰	C _n
I	36-28	0.8	1.3579	—	C ₃
II	45-51	0.4	1.3723	0.6494	C ₄
III	53-55	3.4	1.3718	0.6581	C ₄
IV	68-69	2.7	1.3750	—	—
V	72-78	1.4	1.3711	0.6546	—
VI	80-85	1.4	1.3839	0.6800	C ₁
VII	104-108	1.4	1.3897	0.6801	—
VIII	110-127	7.5	1.3967	0.7154	C ₄
IX	135-152	3.8	1.4059	0.7158	C ₄
X	155-165	4.8	1.4096	0.7272	C ₁
XI	180-200	5.3	1.4163	0.7415	C ₁₁
XII	215-220	3.4	1.4232	0.7500	C ₁₁
XIII	225-241	5.2	1.4273	0.7695	C ₁₁
XIV	247-260	4.8	1.4323	0.7709	C ₁₁
XV	268-280	6.9	1.4362	0.7784	C ₁₁
XVI	288-310	6.6	1.4400	0.7856	C ₁₁
XVII	316-332	9.6	—	0.8019	C ₁₁
Residue	—	11.0	—	—	—
Original condensate	—	—	1.4179	0.7362	—

distillate contained 85.8% of 2-butene and 14.2% of butane. These amounts of 2-butene and butane, which must be taken into account in the investigation of the outgoing gas, are so small that they do not introduce any substantial changes in the composition as calculated above. After being debutanized the condensate had n_D²⁰ 1.4215 and d_A²⁰ 0.7389; the refractive index did not change when the condensate was boiled over sodium for two hours under a short low-temperature column.

The debutanized condensate (90 ml; bromine value 38.9, corresponding to about 37% of unsaturated hydrocarbons) was hydrogenated in presence of platinumized charcoal (3 ml) to which H₂PtCl₆ had been added (4).

After the absorption of 3500 ml (S.T.P) of hydrogen, a further 1 ml of platinumized charcoal was added and a further 150 ml of hydrogen was then absorbed. After being dried over copper sulfate the hydrogenation product had η_{D}^2 1.4178, η_{D}^3 0.7362, and bromine value 0.6. The product (73 ml) was fractionated at 747 mm through a 40-plate column.

About 26% by volume came over below 130°. The fractionation curve is shown in Fig. 2. The residue from the distillation through the column was distilled from a Favorsky flask. All of the fractions collected and their properties are given in Table 3. The intermediate fractions, which amounted to less than 0.3%, are not given in Table 3.

It follows from Table 3 and Fig. 2 that about 30% by volume of the condensate comes over below 152°, and this contains C_6 , C_7 , C_8 , C_9 , and C_{10} hydrocarbons in the proportion of about 1, 6, 9, 8, 4. The pentane (the fraction (Fraction I, b.p. 36-58°, η_{D}^2 1.3879), which formed 0.8% of the condensate, consisted of n-pentane (the literature [5] gives b.p. 36-57°, η_{D}^2 1.3575). Fraction III corresponded most closely in properties to 2-methylpentane (b.p. 60.27°, η_{D}^2 1.3715, η_{D}^3 0.6832 (5)), and Fraction IV, b.p. 68-69°, η_{D}^2 1.3750, η_{D}^3 0.6580, was n-hexane (the literature [5] gives b.p. 68.74°, η_{D}^2 1.3749, η_{D}^3 0.6594). The heptane fraction (Fraction VI) had the constants η_{D}^2 1.3859, η_{D}^3 0.6806, which are somewhat low in comparison with those of n-heptane (b.p. 98.49°, η_{D}^2 1.3877, η_{D}^3 0.6837 (5)).

Of the heptane isomers having one side chain only 2-methylhexane has lower constants (b.p. 90.05°, η_{D}^2 1.3849, η_{D}^3 0.6782 (5)) than n-heptane, and we may therefore assume that Fraction VI contains some of this hydrocarbon. Fraction VIII, b.p. 110-127°, η_{D}^2 1.3967, η_{D}^3 0.7013, is close in properties to n-octane (b.p. 125.67°, η_{D}^2 1.3974, η_{D}^3 0.7025 (5)), but its constants are somewhat low. In this case only 2-methylheptane (b.p. 117.65°, η_{D}^2 1.3950, η_{D}^3 0.6979 (5)) has lower constants than n-octane, and it may be assumed that it is present in Fraction VIII. This is confirmed also by the presence on the fractionation curve (Fig. 2) of a step corresponding to n-octane. We are not here taking account of more highly branched hydrocarbons because their formation is not very likely under the conditions of reaction.

When Fractions VIII and VI and a mixture of Fractions III and IV were investigated by the Raman-spectrum method*, only C_6 , C_7 , and C_8 -n-alkanes were detected, the corresponding characteristic wave numbers (cm^{-1}) being: Fraction VIII - 813, 860, 878, 895, 1030, 1044, 1062, 1085, 1140, 1304, 1440, 1460; Fraction VI - 826, 893, 901, 1040, 1140 [1].

It will be clear from these results that the hydrocondensation obtained from carbon monoxide and 2-butene consists essentially of normal alkanes, probably together with a small amount of 2-methylalkanes. The results show that 2-butene itself participates only to an insignificant extent in the hydrocondensation reaction, the reaction products being mainly formed from a 1-alkene, i.e., from 1-butene, which is doubtless formed by the catalytic isomerization of 2-butene.

In the preceding paper [3] we studied the catalytic isomerization of 2-butene into 1-butene and of 1-butene into 2-butene under the conditions of the hydrocondensation of carbon monoxide with olefins, both in presence and in absence of hydrogen, but always in absence of carbon monoxide. It was shown that the hydrocondensation catalyst is active in the reaction of double-bond displacement only when hydrogen is present, 1-butene in admixture with 10% of hydrogen being partially isomerized into 2-butene with formation of an approximately equimolecular mixture of 1-butene and 2-butene. On the other hand, in experiments with 2-butene passed in admixture with 10 or 26% of hydrogen over the hydrocondensation catalyst under the same conditions, no 1-butene was found in the outgoing gas, in spite of the fact that there should be about 10% present in an equilibrium mixture. In the isomerization experiments, both on 1-butene and on 2-butene, a considerable proportion of the olefin remained adsorbed on the catalyst surface and some of it was hydrogenated to butane (somewhat more in the 1-butene experiments than in those on 2-butene).

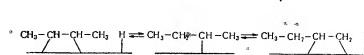
The results obtained in the present investigation show quite clearly that, under hydrocondensation conditions, isomerization of 2-butene into 1-butene does occur, but the 1-butene formed (calculation shows that not more than 5-6% can be formed) remains adsorbed on the catalyst surface and then, when it becomes possible to

enter into the reaction of hydrocondensation with carbon monoxide, is converted into high-boiling products; the 2-butene continues to isomerize into 1-butene.

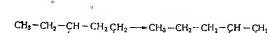
Hence, the products of the hydrocondensation of 2-butene with carbon monoxide are really formed from the 1-butene produced by displacement of the double bond of 2-butene. It is interesting that the whole of the 1-butene formed in this way takes part in the hydrocondensation reaction, for, as we saw above, only 2-butene is present in the outgoing gas.

The formation of some of the products of the hydrocondensation of carbon monoxide with 2-butene can be expressed schematically as follows:

1) Isomerization of 2-butene into 1-butene [6]:

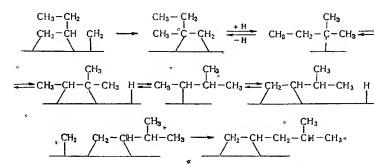


2) Formation of pentene:



In a previous investigation [7] 5.5-7% of a C_5 fraction was obtained in the hydrocondensation of 1-hexene with carbon monoxide, and this could be formed only by the hydrotacking of the original 1-hexene and its transformation products. In experiments with 2-butene in the present investigation, hydrotacking products (about 5° boiling lower than the butenes were again obtained). It is probable that olefins containing five or more carbon atoms can also be formed to some extent by the hydrotacking of hydrocarbons of higher molecular weight formed in the reaction.

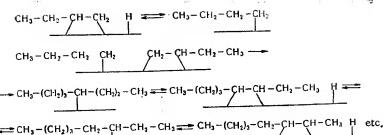
3) The formation of 2-methylpentane, 2-methylhexane, and 2-methylheptane, which appear to be formed in small amounts, can be represented as follows, the starting substance being 1-butene [8]:



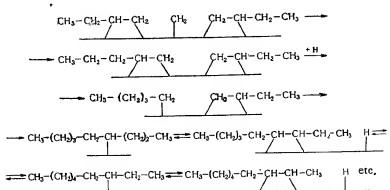
Hydrogenation of the adsorbed isomeric methylpentenes give 2-methylpentane, 2-methylhexane and 2-methylheptane can be formed from methylpentene by analogous reactions, and these may arise also by the polymerization and copolymerization of olefins formed by hydrotacking.

4) Formation of octene by dimerization [8]:

* The spectra were determined by Yu. P. Egorov, to whom we express our thanks.



5) Formation of nonene (8):



The course of the formation of hydrocondensation products is much more complex than it would appear from these schemes. CH_3 radicals on the surface probably attack hydrogen and make it possible for a semi-hydrogenated state to arise, e.g. of the type $\text{R}-\text{CH}_2-\overset{\cdot}{\text{CH}_2}$, which is able to interact readily with adsorbed olefin molecules.

SUMMARY

1. An investigation was made on the catalytic hydrocondensation of carbon monoxide with 2-butene at 190° and atmospheric pressure, 4-6% of carbon monoxide being present in the original mixture, which consisted of 70-75% of 2-butene and 21-26% of hydrogen. The yield of organic condensate amounted to 542.3 ml per cu.m., or 55.5 ml/liter, hour.

2. The main reaction products were n-alkanes, probably with some admixture of 2-methylalkanes.

3. The results show that in the hydrocondensation of carbon monoxide with 2-butene, the latter isomerizes into 1-butene, which then reacts with hydrogen and carbon monoxide giving predominantly n-alkanes.

4. These results confirm views advanced previously by the effect that 2-butene, like 1-butene, undergoes isomerization by double-bond displacement under the conditions of hydrocondensation in presence of hydrogen.

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CHEMICAL CHANGES PRODUCED IN THE CELLULOSE
MACROMOLECULE BY OXIDIZING AGENTS

COMMUNICATION 10. OXIDATION OF HYDROXY COMPOUNDS OF LOW
MOLECULAR WEIGHT WITH NITROGEN DIOXIDE

E. D. Kaverzneva, V. I. Ivanov, and A. S. Salova

In the literature the view is widely held that, in the cold, nitrogen dioxide is a specific oxidant for carbohydrates, in which it attacks primary alcohol groups, but has no effect on secondary alcohol groups. On the basis of this hypothesis, nitrogen dioxide has been used for the preparation of glucosiduronic acids from glucosides [1] in 75-80% yield and dicarboxylic acids from monosaccharides in 44% yield [2]. On the basis of the same hypothesis, Kenyon has stated that cellulose oxidized with nitrogen dioxide is a "cellulosic acid", i.e., that the C-6 primary alcohol groups of the glucose residues are oxidized to carboxyl groups and no other oxidative changes occur [3].

Doubt has been thrown on the correctness of this assertion by us, by Nevell [4], and by Nabar and Padmanathan [5]. According to our work [6], in the preparation of oxycelluloses by NO_2 oxidation, not only are the primary alcohol groups oxidized, but also the secondary alcohol groups, which are converted into keto groups. It was therefore of interest to obtain a more precise idea of the course of the oxidative reactions occurring when nitrogen dioxide reacts with various hydroxy compounds of low molecular weight. For this purpose we selected isopropyl alcohol, ethylene glycol, 1,2-propanediol, and methyl glucoside.

EXPERIMENTAL

The hydroxy compounds were oxidized with nitrogen dioxide in carbon tetrachloride solution at not above 20°, the medium either being anhydrous or having an addition of 5% of water on the weight of hydroxy compound so that the effect of water on the course of the reaction could be determined. The amount of nitrogen dioxide (distilled over phosphoric oxide and oxidized to completion in a current of oxygen; b.p. 21.2-21.5°) brought into reaction was 50% of the amount calculated for the complete oxidation of all primary alcohol groups to carboxyls and all secondary alcohol groups to keto groups. The hydroxy compounds were dried and distilled before reaction. Isopropyl alcohol boiled at 92.1° and contained 0.1% of acetone; ethylene glycol had b.p. 195°, n_{D}^2 1.4319, 1,2-propanediol had b.p. 104° (30 mm), n_{D}^2 1.4330; methyl glucoside melted at 166°.

The reaction was carried out in a three-necked flask fitted with condenser, stirrer, and dropping funnel. A weighed amount (0.2-0.5 mole) of the hydroxy compound, contained in 50 ml of carbon tetrachloride, was introduced into the flask, and a solution of the required amount of nitrogen dioxide in 50 ml of carbon tetrachloride was added through the dropping funnel. Heat was evolved, and the mixture was cooled so that the temperature did not rise above 20°. The reaction mixture was stirred for 1-2 hours, and then set aside at room temperature for 20 hours. Oily drops generally floated on the top of the greenish-yellow solution. After 20-24 hours the reaction was brought to an end, the excess of nitrogen oxides being removed in the cold under reduced pressure. The solution was poured into water, the liquid layers were separated, and the carbon tetrachloride layer was washed several times with water. The aqueous and carbon tetrachloride layers were investigated separately.

TABLE 1
Summary of Oxidation Experiments

Experiment No.	Composition of reaction mixture (moles)	Experimental conditions	Water-soluble fraction Carbonyl compounds (mg-equiv)	Acids (mg-equiv)	Total yield from aqueous fraction and dry distillate CCl_4 fraction (%)
1	Isopropyl alcohol 0.52, NO_2 0.26	28*, 25 hours	Acetone 11.5	Formic acid 0.3, acetic acid	Acetone 4.7
2	Isopropyl alcohol 0.52, NO_2 0.26, H_2O 0.08	28*, 25 hours	Acetone 29.6	Formic acid 0.16, acetic acid	Acetone 12
3	Ethyleneglycol 0.25, NO_2 0.50	14*, 24 hours	Glycolaldehyde traces	Glycolic acid Present, oxalic acid traces	-
4	Ethyleneglycol 0.25, NO_2 0.50, H_2O 0.15	14*, 24 hours	Glycolaldehyde traces	Glycolic acid Present, oxalic acid 3.1	Oxalic acid 1.26
5	1,2-Propanediol 0.40, NO_2 0.60	20*, 24 hours	Hydroxyacetone 0.01	Pyruvic acid present	Hydroxyacetone 0.035
6	1,2-Propanediol 0.40, NO_2 0.60, H_2O 0.17	20*, 24 hours	Hydroxyacetone 0.04	Pyruvic acid present	Hydroxyacetone 0.01
7	Methyl glucoside 0.127, NO_2 0.39	20*, 24 hours	Hydroxy keto compound 1.24	Methyl glucosidic acid 0.20	Glucosidic acid 0.17, keto compound 1.24
8	Methyl glucoside 0.09, NO_2 0.33, H_2O 0.04	20*, 24 hours	Hydroxy keto compound 9.6	Methyl glucosidic acid 6.83	Glucosidic acid 7.9**, keto compound derived from glucosidic acid 10.8

* 2.34 g of barium salt was isolated.

** 1.52 g of calcium salt was isolated.

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Investigation of Water-soluble Fraction. The total acidity was determined, and part of the neutralized aqueous solution was vacuum-distilled, the volatile aldehydes being trapped in sodium bisulfite solution. The residue was then acidified, and the volatile acids were trapped in 0.5 N NaOH. Aldehydes and volatile acids (formic, acetic, nitro, and nitric) were determined in the respective distillates. The same determinations were carried out with part of the solution in which nitrite ions had been destroyed by addition of urea. The residue from the distillation contained compounds of low volatility, which were identified by the preparation of derivatives, by quantitative methods of estimation, and, in some cases, by paper chromatography. The results of the investigation of the composition of the oxidation products are given in Table 1.

Investigation of Reaction Products Soluble in Carbon Tetrachloride. After being carefully washed with water and dried over sodium sulfate, solutions of the reaction products in carbon tetrachloride were yellowish. Nitrite ions were formed when the solutions were treated with alkali. The solutions were investigated for the presence of nitric and nitrous esters before and after hydrolytic treatment with alkali at room temperature. In the analysis, 5-mil portions of the carbon tetrachloride solution were measured into two 100-mil measuring flasks, and 20 ml of water was added to each portion.

Into one of the flasks, 1 ml of 40% NaOH was added in order to hydrolyze the esters. The solutions were allowed to stand for 24 hours at room temperature and then brought to 100 ml with water. Nitric acid was determined in this solution colorimetrically with "disulphophenol" acid [7], and nitrous acid was determined colorimetrically by the 1-naphthol reaction [8]. In some cases, the contents of keto groups and of individual ketones were also determined (Table 2).

TABLE 2
Investigation of Fractions dissolved in Carbon Tetrachloride

Experiment No.	Substance oxidized	Amount of HNO_3 (mg-equiv)		Amount of HNO_2 (mg-equiv)		Found (mg-equiv)	
		Before hydroly- sis	After hydroly- sis	Before hydroly- sis	After hydroly- sis	Before hydroly- sis	After hydroly- sis
1	Isopropyl alcohol	16.9	1.9	Traces	Several times as great	10.1	13.2
2	Isopropyl alcohol in presence of moisture	13.3	2.8	Traces	Ditto	25	32.7
3	Ethyleneglycol	10.8	12.1	Nil	0.20	Nil	Present
4	Ethyleneglycol in presence of moisture	3.5	1.9	2.8	8.7	"	"
5	1,2-Propanediol	NH	0.16	Nil	0.23	Nil	Present
6	1,2-Propanediol in presence of moisture	0.5	2.3	0.19	1.9	"	"
7	Methyl glucoside	NH	NH	Nil	Nil	"	"
8	Methyl glucoside in present of moisture	"	"	"	"	"	"

* In the oxidation of methyl glucoside the nitric esters were in the water-soluble fraction. Before hydrolysis the NO_2 content was nil, and after hydrolysis it was 16 mg-equiv.

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Oxidation of Isopropyl Alcohol. After the oxidation of isopropyl alcohol, acetone was determined in the distillate of the aqueous layer by the salicylaldehyde colorimetric method (Fabini's reaction [9]). This reaction is specific for ketones containing the grouping $-C(H_3)-CO-CH_2-$, and acetaldehyde and alcohols do not interfere.

The yield of acetone corresponded to 4.7% of the isopropyl alcohol taken when water was absent, and to 12% when water was present. The formation of acetone was confirmed by the preparation of its 2,4-dinitrophenylhydrazone, of which 70 mg were obtained, m.p. 125.5° (the literature gives 126°).

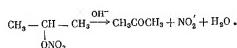
Found % N 23.41 (Dumas)

Calculated % N 23.52

Qualitative reactions showed the presence of formic and acetic acids in the volatile-acid distillate. Quantitative determination of formic acid with mercuric chloride gave 0.3 mg-equiv (0.0005%) for oxidation in anhydrous medium and 0.16 mg-equiv (0.0003%) for oxidation in presence of water.

In the analysis of the fraction soluble in carbon tetrachloride, it was found that it gave a positive reaction for nitrite with the Griess reagent, and the color was more intense when a preliminary treatment with alkali was given. When the solution was made alkaline and allowed to stand, it became acid again owing to the hydrolysis of nitric or nitrous ester. It was established that, after alkaline hydrolysis, the nitric acid content (free and bound as ester) fell and nitrous acid appeared, although this was usually present only in traces before hydrolysis.

Nitrous acid could be formed by hydrolysis of isopropyl nitrite with regeneration of isopropyl alcohol, and also by oxidative hydrolysis of isopropyl nitrate. In the latter case acetone would be formed. Colorimetric determinations showed that, in the experiment under anhydrous conditions, 13.2 mg-equiv of acetone was formed after hydrolysis of the fraction soluble in carbon tetrachloride, and in the experiment in presence of water 32.7 mg-equiv of acetone was formed. There was therefore an appreciable amount of isopropyl nitrate in the carbon tetrachloride solution, and on hydrolysis this was converted into acetone with formation of nitrous acid.



Oxidation of Ethylene Glycol. The aqueous fraction from the oxidation of ethylene glycol did not give aldehyde reaction and therefore did not contain glycolaldehyde. After removal of volatile acids under reduced pressure, oxalic acid was precipitated as the calcium salt in presence of ammonia and ammonium chloride. The precipitate was washed through with dilute hydrochloric acid, and oxalic acid was determined by titration with 0.1 N KMnO_4 .



Fig. 1. Chromatograms: A) experimental solution; B) glycolic acid

In the oxidation in an anhydrous medium, the aqueous fraction contained only traces of oxalic acid, whereas in the experiment in presence of water, 0.140 mg of oxalic acid was found (1.15% on the amount of ethylene glycol taken). Apart from oxalic acid, glycolic acid was detected by paper chromatography (tolvent: a 10 : 2 : 8 mixture of butyl alcohol, formic acid, and water; developer: Bromophenol blue) (Fig. 1).

When the fraction soluble in carbon tetrachloride was hydrolyzed with 2% caustic soda in the cold, nitrous acid was formed and the solution gave a positive result with Schiff's reagent. In an acid medium no hydrolysis occurred and no nitrous acid was formed.

Oxidation of 1,2-Propanediol. The aqueous fraction from the oxidation of 1,2-propanediol gave no reaction with Schiff's reagent. The reaction with Fehling's solution was positive in the cold, as also was Benedict's reaction for the hydroxy ketone grouping. Practically no volatile acids were formed. The residue remaining after the removal of volatile compounds was heated with an alcoholic solution of 2,4-dinitrophenyl-

hydrazine and hydrogen chloride, and an osazone, m.p. 299.5-300° (after recrystallization from ethyl acetate), was isolated. For the osazone of hydroxyacetone the literature gives m.p. 300°. In Experiment 5 the amount of osazone isolated corresponded to 0.67 mg of hydroxyacetone, and in Experiment 6 it corresponded to 2.72 mg.

Hydrazones of keto acids were extracted by means of sodium carbonate solution from the mother liquor left after the crystallization of the osazone of hydroxyacetone. After acidification and extraction of the solution with ethyl acetate, a small amount of hydrazones was obtained. In order to test for the presence of the 2,4-dinitrophenylhydrazone of pyruvic acid, the material was investigated chromatographically against a synthetic preparation (m.p. 218°) obtained by the condensation of pyruvic acid with 2,4-dinitrophenylhydrazine. In the separation on paper (solvent: butyl alcohol saturated with 3% ammonia solution), two pairs of spots were obtained; these corresponded exactly with one another and with data in the literature [10], according to which this hydrazone, like free pyruvic acid, gives two spots in paper chromatography (Fig. 2).

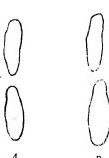


Fig. 2. Chromatograms: A) experimental solution; B) pyruvic acid



Fig. 3. Chromatograms: A) lactic acid; B) nitric acid; C) experimental solution; D) pyruvic acid

Direct chromatographic separation of the aqueous fraction of acids on paper showed the presence of pyruvic and nitric acids in the oxidation products of 1,2-propanediol; no lactic acid was detected (Fig. 3). In the fraction that dissolved in carbon tetrachloride, an appreciable amount of nitrous acid was formed after hydrolysis with 2% caustic soda in the cold. Before hydrolysis the colorimetric reaction with salicylaldehyde for hydroxyacetone was negative, but after hydrolysis it was positive, thus indicating the formation of hydroxyacetone in the hydrolysis.

Oxidation of Methyl α -Glucoside. In the oxidation, 2.5 moles of nitrogen dioxide were taken for each mole of the glucoside. As oxidation proceeded the appearance of the suspension of methyl glucoside in carbon tetrachloride changed and it gradually became a sticky greenish syrup. This was allowed to stand for 24 hours; nitrogen oxides were removed in the cold under reduced pressure, and the product was treated with water, yielding an aqueous layer, which contained the bulk of the reaction products, and a carbon tetrachloride layer, which did not contain an appreciable amount of oxidized compounds.

There were no aldehydes and volatile organic acids in the aqueous layer. After the content of nitric and nitrous acids had been taken into account, the acidity of the aqueous layer was still high, which indicated that much of the glucoside had been oxidized. The aqueous layer gave an intense reaction with Benedict's reagent for α -hydroxy ketone groupings [11], the amount of which was found to be 1.24 mg-equiv (0.97% of the amount calculated for the oxidation of one alcohol group) for reaction in an anhydrous medium and 9.6 mg-equiv (10.8%) for reaction in presence of water. When allowed to stand in an alkaline medium, the aqueous fraction became acid, the extent of the acidification being 12% of the acidity of the original solution. As acidity developed there was an increase in the content of nitrite ions.

Methyl glucosiduronic acid was isolated in Experiment 7 as the barium salt (1.74 g from one half of the volume of the reaction products) and in Experiment 8

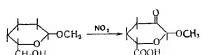
as the calcium salt (1.52 g). The salts were not purified from inorganic salts, but were used directly for the preparation of osazones in order to prove the presence of keto derivatives. According to the analysis of the barium salt, it contained hydroxy ketone groupings in an amount corresponding to 2.7% admixture of an oxidized methyl glucosiduronic acid containing a keto group to the main mass of methyl glucosiduronic acid.

When the barium and calcium salts were treated with a solution of 2,4-dinitrophenylhydrazine in aqueous 2 N HCl at 5-7°, osazones of high melting point (above 340°) were obtained; they gave a bluish-violet color with alkalis, and they were soluble in ethyl acetate.

Found %: N 19.74 (osazone from Ba salt)
Found %: N 19.57; 19.93 (osazone from Ca salt)
Calculated %: N 19.86

The corresponding osazone of glucuronic acid, which could be formed if the glucoside methyl were to be eliminated, contains 20.30% N, i.e., appreciably more than the amount found.

A more complete analysis of the osazones obtained could not be carried out owing to their small amount. All of these facts lend a considerable measure of probability to the suggestion that the glucosiduronic acid was admixed with some oxidized glucosiduronic acid containing a keto group formed by the oxidation of a secondary alcohol group of methyl glucoside.

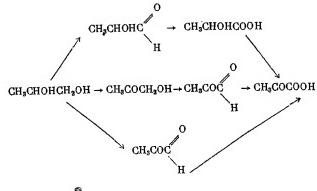


Discussion of Experimental Results

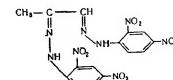
Oxidation of hydroxy compounds with nitrogen dioxide under the given experimental conditions - in the cold for a comparatively short time (24 hours) with half of the amount of nitrogen dioxide that would be theoretically required for complete oxidation - does not result in far-reaching decomposition. On this account examination of the reaction products enables us to determine the primary direction in which the oxidation processes proceed.

The formation of appreciable amounts of acetone (up to 12%) from isopropyl alcohol and of hydroxyacetone from 1,2-propanediol, and also the formation of hydroxy ketone groupings in the oxidation of methyl glucoside, shows that secondary alcohol groups are oxidized by nitrogen dioxide under the given conditions. Moreover, oxidation does not stop at this stage, but continues further with scission of a C-C bond, as indicated by the presence of small amounts of formic and acetic acids in the reaction products.

In the oxidation of ethylene glycol the successive stages in the oxidation of the two alcohol groups can be observed, glycolic and oxalic acids being formed. In the oxidation of 1,2-propanediol, the number of possible oxidation products increases.

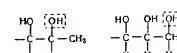


From the reaction products an osazone was isolated which corresponds in analysis to:



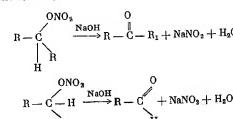
This osazone could be formed from any of the three carbonyl compounds given in the scheme. However, as the solution does not give a reaction for aldehyde groups while giving a strongly marked reaction for hydroxy ketone groupings, the question is resolved in favor of hydroxyacetone as one of the primary products of the oxidation of 1,2-propanediol with nitrogen dioxide. Direct colorimetric determination of hydroxyacetone in the reaction products gave a content corresponding to 0.002-0.01% of the theoretically possible content for the oxidation of one hydroxy group per molecule. Since 1,2-propanediol has a glycol grouping in which one hydroxyl is primary and the other secondary, it was of interest to determine which of the two alcohol groups is preferentially oxidized. One might expect that lactic acid would be the main reaction product, and pyruvic acid would be a secondary product. However, the presence among the reaction products of hydroxyacetone and pyruvic acid and the absence of detectable amounts of lactic acid indicate that the oxidation processes proceed in a different way, the predominating process being the oxidation of the secondary alcohol group. A different picture is to be observed in the oxidation of methyl glucoside; here, the main direction of reaction in an anhydrous medium is the oxidation of the primary alcohol group at the terminal carbon atom (to the extent of 8%). The oxidation of secondary alcohol group occurs only to a slight extent (not more than 1%), as our experiments have shown, and only in the presence of water - when far-reaching decomposition sets in - are hydroxy ketone groupings formed to an appreciably greater extent (10-11%).

The effect of molecular structure is to be seen in this difference in order of oxidation: when there is a methyl group in proximity to a hydroxyl, the secondary alcohol group is more readily oxidized, but in carbohydrates, in which all carbons carry OH groups, the primary alcohol group is oxidized first:



Hence, 1,2-propanediol gives hydroxyacetone as main product, whereas methyl glucoside gives methyl glucosiduronic acid.

As we have shown, in the fraction of the oxidation products that passes into carbon tetrachloride (or into water, in the case of methyl glucoside), there are compounds that eliminate nitrous acid when treated with alkali in the cold. These could be nitro or nitric ester of oxidizable alcohols. As it is found that hydrolysis is accompanied by the formation of ketones or aldehydes (acetone from isopropyl alcohol, hydroxyacetone from 1,2-propanediol, and an aldehyde from ethylene glycol). It is probable that oxidative hydrolysis of nitric esters occurs, in accordance with the scheme:



Hence, the mechanism proposed by Kenyon [12], in which the oxidation of cellulose proceeds with intermediate formation of nitric ester, can probably be extended to the oxidation of hydroxy compounds of low molecular weight with nitrogen dioxide. The general character of this reaction follows also from Titov's investigation [13] which show that, in the nitration of hydrocarbons, in addition to nitro derivatives nitric and the nitrates of the corresponding alcohols are formed and are subsequently oxidized. In our experiments, the effect of water was very marked: in presence of moisture oxidation always proceeded more vigorously and the yields of oxidation products were higher than in a dry anhydrous solvent. This fact can also be interpreted in the light of the proposed oxidation mechanism, in accordance with which the primary stage of the reaction is the formation of a nitric ester by the action of nitric acid formed from nitrogen dioxide and traces of moisture.

* SUMMARY

1. The main product in the oxidation of isopropyl alcohol by nitrogen dioxide at room temperature is acetone. In different experiments the yield of acetone varies from 2% to 12% on the amount of alcohol taken.

2. The oxidation of ethylene glycol with nitrogen dioxide proceeds in such a way that it is difficult to characterize the intermediate products in the oxidation. The process rapidly reaches the stage of oxalic acid formation. Oxalic and glycolic acids were identified.

3. Among the oxidation products of 1,2-propanediol, hydroxyacetone and pyruvic acid were identified. No lactic acid was found. This indicates that the predominating process is the oxidation of secondary alcohol groups.

4. A study of the oxidation of methyl α -D-glucoside with nitrogen dioxide under the same conditions showed that not only primary, but also secondary alcohol groups are oxidized. In the methyl glucosiduronic acid obtained from the products as the barium and calcium salts, another compound, containing a hydroxy ketone grouping, was present as impurity. An osazone was prepared from this compound, and it corresponded in analysis to the osazone of an oxidized methyl glucosiduronic acid containing a keto group.

5. It was established that the process of oxidizing alcohols of low molecular weight and methyl glucoside with nitrogen dioxide proceeds through the stage of a nitric ester, which undergoes oxidative hydrolysis with elimination of nitrous acid.

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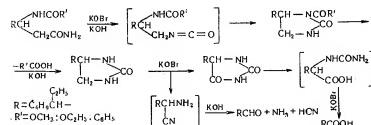
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Academy of Sciences of the USSR

NEW DATA ON THE HOFMANN REACTION

COMMUNICATION 4. ACTION OF HYPOBROMITE ON DIASTEREOISOMERIC
3-(ACYLA MINO)-4-ETHYLOCTANAMIDES

V. M. Rodionov*, V. K. Zvorykina, and N. E. Kozhevnikova

In previous investigations on the Hofmann reaction of amides of β -acylamino acids, namely derivatives of 3-aminoacrylic [1], β -aminohydrocinnamic [2], and β -amino-3,4-methylenedioxycinnamic [3] acids, it was shown that acids containing aromatic and aliphatic radicals behave differently. Although in the first stage of the reaction the same type of product is formed in both cases by intramolecular rearrangement of the isocyanate - the corresponding 1-acyl-5-alkyl(or aryl)-2-imidazolidinone - the second stage - hydrolysis of the acyl group and formation of a 5-alkyl(or aryl)-2-imidazolidinone - proceeds considerably more rapidly in the case of an amino acid containing an aromatic radical. The further transformation of the imidazolidinone, leading finally to a carboxylic acid, proceeds in the case of a β -amino acid containing an aliphatic radical, through the stages of the formation of an alkylhydantoin, an α -ureido acid, and an α -amino acid, but in the case of a β -amino acid containing an aromatic radical through the intermediate formation of an amynurea and a 5-aryloxy- Δ^4 -1,3,4-oxadiazolin-2-one.



With the object of confirming previous observations, we carried out Hofmann's reaction with amides of benzoyl and alkoxy carbonyl derivatives of two diastereoisomeric 3-amino-4-ethyloctanoic acids which we have synthesized and denoted by the symbols A_1 and A_2 [4]. Reaction with the benzoyl derivative stopped at the stage of the imidazolidinone. As by-products, both isomers gave high-melting neutral substances corresponding in analysis to alkylarylanilines. Reaction of the isocyanate in this direction is generally observed when the amides are sparingly soluble, and we have observed it also in a previous investigation [5]. When the Hofmann reaction was carried out with amides of alkoxy carbonyl derivatives of the isomers A_1 and A_2 , products obtained were the 1-alkoxy carbonyl-5-(1-ethylpentyl)-2-imidazolidinone, 4-(1-ethylpentyl)-2-imidazolidinone, 5-(1-ethylpentyl)-hydantoin, and 2-ethylhexanoic acid. Also, when the oil remaining after the separation of these compounds was hydrolyzed, the presence of 2-ethylhexanal, ammonia, and hydrogen cyanide was detected in the product. From

* Deceased.

this it may be inferred that, as in the case of other aliphatic β -amino acids, for the new representatives of this class of compound that we have studied, the process proceeds in accordance with the general scheme that we proposed in a previous paper [1].

EXPERIMENTAL

Hofmann Reaction with 3-Benzamido-4-ethyloctanamide (A_2 Isomer)

The amide (4 g) was gradually added to a hypobromite solution prepared from 1.75 g of bromine, 6.45 g of caustic potash, and 45 ml of water at -7° to -10° . When solution was complete, stirring was continued for one hour. The solution was then heated to 65° and cooled rapidly. The solution and the precipitate that had formed were treated with ether.

Isolation of Benzoic Acid. Acidification of the alkaline solution yielded 0.35 g of benzoic acid, m.p. 122 $^\circ$.

Isolation of Substance of M.p. 219 $^\circ$. The ether-insoluble precipitate was boiled with water and crystallized from alcohol. The product, amounting to 0.4 g, melted at 219 $^\circ$ (fine colorless prisms).

Found %: C 71.02; 70.93; H 8.74; 8.67; N 9.30; 9.45
Calculated %: C 70.59; H 8.65; N 9.67

Isolation of 1-Benzoyl-5-(1-ethylpentyl)-2-imidazolidinone A_2 . The ether solution was extracted several times with 12% hydrochloric acid, washed, first with water, then with caustic soda solution, and again with water, and dried with sodium sulfate. After part of the ether had been distilled off, 1.2 g of a substance of m.p. 153 $^\circ$, was obtained.

Found %: C 70.98; 70.79; H 8.59; 8.36; N 9.70; 9.59
Calculated %: C 70.83; H 8.33; N 9.72

Further removal of ether enabled about 0.5 g more of the imidazolidinone A_2 to be isolated. When ether was removed completely there remained an oil, and treatment of this with a mixture of diethyl ether and petroleum ether gave 0.04 g of a substance melting at 148 $^\circ$ which did not appear to be the imidazolidinone A_2 isolated as indicated above.

Found %: N 11.48; 11.51

This substance was not studied in detail.

Isolation of 4-(1-Ethylpentyl)-2-imidazolidinone A_2 . Cooling of the hydrochloric acid solution and careful addition of solid caustic potash yielded 0.29 g of a substance of m.p. 140-141 $^\circ$ (needles from a mixture of diethyl ether and petroleum ether).

Found %: C 65.31; H 10.50; N 15.47; 15.39
Calculated %: C 65.21; H 10.86; N 15.21

Hydrolysis of 1-Benzoyl-5-(1-ethylpentyl)-2-imidazolidinone A_2 . Heating of 0.3 g of the benzoylimidazolidinone A_2 with 20% caustic soda for four hours in a water bath yielded 0.06 g of benzoic acid, m.p. 121 $^\circ$, 0.07 g of the above-described 4-(1-ethylpentyl)-2-imidazolidinone, m.p. 139-140 $^\circ$, and 0.01 g of the above-described substance of m.p. 148 $^\circ$.

Hofmann Reaction with 3-Benzamido-4-ethyloctanamide (A_1 Isomer)

When the reaction was carried out with 6.81 g of amide under the conditions described for the A_2 isomer, acidification of the alkaline solution yielded 0.21 g of benzoic acid. The ether-insoluble precipitate gave 0.43 g of a substance of m.p. 204 $^\circ$.

* Experimental investigation of the Hofmann reaction applied to 3-benzamido-4-ethyloctanamide A_1 was carried out by N. E. Kochevnikova. All of the remaining experimental work was carried out by V. K. Zvorykina.

Found %: C 71.83; 72.01; H 8.85; 9.06; N 9.76; 9.69

The ether solution yielded 2.65 g of 1-benzoyl-5-(1-ethylpentyl)-2-imidazolidinone A_1 , m.p. 141-142 $^\circ$ (needles from ether). A mixture with the A_2 isomer melted at 114-116 $^\circ$.

Found %: C 70.64; 70.52; H 8.58; 8.52; N 9.85; 9.92

The hydrochloric acid solution yielded 0.25 g of 4-(1-ethylpentyl)-2-imidazolidinone A_1 , m.p. 141-142 $^\circ$ (colorless needles from ether). A mixture with the A_2 imidazolidinone melted at 117-123 $^\circ$.

Found %: C 65.15; 65.28; H 10.92; 10.99; N 15.51; 15.34

Hydrolysis of 1-benzoyl-5-(1-ethylpentyl)-2-imidazolidinone A_1 gave benzoic acid and 4-(1-ethylpentyl)-2-imidazolidinone A_1 , m.p. 139-140 $^\circ$.

Hofmann Reaction with 4-Ethyl-3-(methoxycarbonylamino)octanamide (A_1 Isomer)

The amide (20 g) was added in small portions with stirring to a cooled (-8°) solution of hypobromite prepared from 40 g of caustic potash, 280 ml of water, and 10.3 ml of bromine. When solution was complete (about three hours), stirring was continued for one hour at room temperature and the flask was then transferred to a water bath and the temperature raised to 65 $^\circ$ (at 55 $^\circ$ a spontaneous rise in temperature occurred). The flask was then rapidly immersed in a cooling mixture. The alkaline solution containing precipitated oil was extracted with ether, and the ether extract was extracted several times with 12% hydrochloric acid.

Isolation of 5-(1-Ethylpentyl)-hydantoin A_1 and 2-Ethylhexanoic Acid. When the alkaline solution was acidified an oil separated and was extracted with ether; the ether solution was washed with water and dried with sodium sulfate. After removal of ether there remained 1.3 g of oil, which partially crystallized; when this was treated with 10 ml of heptane, crystals were precipitated, which were twice recrystallized from an alkaline solution with acid and then recrystallized from water. The yield of the hydantoin A_1 was 0.09 g, m.p. 140-141 $^\circ$.

Found %: C 60.66; 60.22; H 9.20; 9.03; N 14.36; 14.25
Calculated %: C 60.80; H 9.09; N 14.14

When the heptane was distilled off, 0.8 g of liquid 2-ethylhexanoic acid remained; it was characterized as its amide, m.p. 104-105 $^\circ$.

Isolation of 4-(1-Ethylpentyl)-2-imidazolidinone A_{1L} . The hydrochloric acid solution was rendered alkaline with solid potassium hydroxide, cooling being applied. The imidazolidinone obtained (0.75 g) melted at 141-142 $^\circ$ (needles from ether) and was identical with that described above.

Isolation of 5-(1-Ethylpentyl)-1-methoxycarbonyl-2-imidazolidinone A_1 . After removal of ether, 9 g of oil was obtained, and this crystallized when seeded with 4-(1-ethylpentyl)-2-imidazolidinone. When a little ether was added, 1.2 g of the imidazolidinone A_1 was precipitated. Addition of heptane to the filtrate resulted in the precipitation of a further 0.2 g of the same substance, and after several hours the clear filtrate gave a precipitate of 1.19 g of 5-(1-ethylpentyl)-1-methoxycarbonyl-2-imidazolidinone A_1 , m.p. 84.5-85 $^\circ$ (from a mixture of diethyl ether and petroleum ether). After the hydrolysis of this compound by boiling it with 20% caustic soda, 4-(1-ethylpentyl)-2-imidazolidinone A_1 was isolated.

Found %: C 59.68; 59.47; H 9.37; 9.45; N 11.79; 11.69
Calculated %: C 59.50; H 9.09; N 11.57

The oil remaining after the separation of the imidazolidinones was hydrolyzed by heating it with 7.5% caustic soda solution. It was shown that hydrogen cyanide, ammonia, and 2-ethylhexanal (identified as the di-nitrophenylhydrazone) were formed.

Hofmann Reaction with 3-(Ethoxycarbonylamino)-4-ethyloctanamide (A_1 Isomer)

The reaction was carried out with 11 g of the amide. The experimental conditions and the methods of isolating the products were similar to those described for the analogous A_1 compound.

Isolation of 5-(1-Ethylpentyl)hydantoin A₁ and 2-Ethylhexanoic Acid. When the alkaline solution was acidified, an oil was precipitated, and when petroleum ether was added to this, 0.072 g of the hydantoin A₂, m.p. 172°, was obtained (purification as for the A₁ isomer).

Found %: C 60.49; H 9.37; N 9.13; N 13.90; 14.14

C₉H₁₆O₂N₂

Calculated %: C 60.60; H 9.09; N 14.14

After removal of petroleum ether there remained an oil. Steam distillation of this yielded 0.17 g of 2-ethylhexanoic acid, which was identified as the amide.

Isolation of 4-(1-Ethylpentyl)-2-imidazolidinone A₂. The hydrochloric acid extract yielded 1.33 g of the imidazolidinone A₂, m.p. 140-141°, already described above.

Isolation of 1-Ethoxycarbonyl-5-(1-ethylpentyl)-2-imidazolidinone A₂. After partial removal of ether the solution gave 1.15 g of 1-ethoxycarbonyl-5-(1-ethylpentyl)-2-imidazolidinone A₂, m.p. 148° (colorless plates from ether). Its alkaline hydrolysis gave 4-(1-ethylpentyl)-2-imidazolidinone A₂, m.p. 140°.

After complete removal of ether, 6 g of a noncrystallizing oil was obtained. One half of this was hydrolyzed with 7% caustic soda solution, and the formation of hydrogen cyanide, ammonia, and 2-ethylhexanal was established. In addition, 2.3 g of 4-(1-ethylpentyl)-2-imidazolidinone A₂, m.p. 139-140°, was isolated.

SUMMARY

1. A study was made of the action of hypobromite on the diastereoisomers A₁ and A₂ of 3-benzamido- and 3-(alkoxycarbonylamo)-4-ethyloctanamides,

2. From the products obtained from the benzamido compounds, the stereoisomeric 4-(1-ethylpentyl)-2-imidazolidinones and 1-benzoyl-5-(1-ethylpentyl)-2-imidazolidinones, and also benzoic acid, were isolated.

3. From the products obtained from the alkoxy carbonylaminocompounds, the stereoisomeric 1-alkoxy-carbonyl-5-(1-ethylpentyl)-2-imidazolidinones, 4-(1-ethylpentyl)-2-imidazolidinones, and 5-(1-ethylpentyl)-hydantoins, and also 2-ethylhexanoic acid, were isolated. When the oil remaining after the separation of the above compounds was hydrolyzed, hydrogen cyanide, ammonia, and 2-ethylhexanal were present among the products.

4. The results obtained confirm the correctness of the scheme that we have proposed previously for the Hofmann reaction with amides of acylated β -amino acids.

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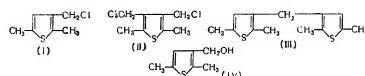
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* T.P. = C. B. Translation pagination.

CHLOROMETHYLATION OF 2,5-DIMETHYLIOPHENE

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Chloromethylation is one of those reactions that are readily affected by various factors. Change of temperature or condensing agent, replacement of formaldehyde by paraformaldehyde, etc., may not only reduce or increase the yield of the product, but may also alter its identity. Lock, in his detailed investigation of the chloromethylation of benzene [1], showed, in particular, the dependence of the yield of benzyl chloride on the zinc chloride content of the reaction mixture and on the duration of the process: the yield of benzyl chloride attains a maximum value (70%) in a certain interval of time and then falls almost to zero as the duration of the experiment increases, this being accompanied by a rapid increase in the yield of diphenylmethane. The peculiar "sensitivity" of this reaction may be the cause of discrepancies in results on chloromethylation obtained by different investigators. As an example we may point out that Lock could not confirm Tschunkur and Echler's results on the synthesis of benzyl chloride by the chloromethylation method. We came across a similar situation in the chloromethylation of 2,5-dimethylthiophene by the action of formaldehyde and hydrogen chloride in hydrochloric acid under cooling in accordance with the procedure of Huo-Hoi and Nguyen Hoan [2]. According to these investigators, under these conditions a little 3-(chloromethyl)-2,5-dimethylthiophene is formed, but the main product is 3,3'-methylenebis(2,5-dimethylthiophene) (III), m.p. 72°. In our experiments we obtained approximately equal amounts of the mono(chloromethyl) derivative (I) and 3,4-bis(chloromethyl)-2,5-dimethylthiophene (II), but did not succeed in isolating any of the substituted methylenedithiophene (IV) of m.p. 72°.

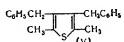


The same two compounds (I) and (II), but in somewhat different proportions, were formed in the chloromethylation of 2,5-dimethylthiophene with chloromethyl methyl ether in glacial acetic acid. In order to confirm the structure of the compound that we regarded as 3-(chloromethyl)-2,5-dimethylthiophene, it was converted via the acetoxyethyl compound into the corresponding alcohol, which, according to its composition and the properties of the urethan derived from it, was identical with 2,5-dimethyl-3-thiophenemethanol (IV), which was prepared by Brown and Blanchette [3] by the reduction of 2,5-dimethyl-3-thiophene-carboxaldehyde. The compound (II), the product of the bis(chloromethylation) of 2,5-dimethylthiophene, was obtained in a yield of about 65% by the chloromethylation of 2,5-dimethylthiophene with paraformaldehyde and hydrogen chloride at 50°, i.e., under conditions almost identical with those described by Gaertner and Tonkin [4]. It must be pointed out that, in this case also, we failed to detect a product of chlorination corresponding to the methylene-dithiophene of structure (IV). We isolated a very small amount of a chlorine-containing product melting at 173°, which was identical in properties with the substance obtained by the chloromethylation of a compound that we had isolated in the course of this work (see below); this latter compound melts at 48.5° and corresponds in composition to the compound (III) mentioned above.

We repeatedly prepared the bis(chloromethyl)dithiophene (II) by the method indicated, and in all of the experiments it melted, after recrystallization, at 67-68.5°; sublimation did not affect its melting point.

On the other hand, in the paper cited by Gaertner and Tonkyn, a melting point of 73.4° is given for 3,4-bischloromethyl-1,2,5-dimethylthiophene. This discrepancy might be caused by the constant presence of an impurity, which could arise from the fact that we did not prepare the original dimethylthiophene from 2,5-hexanedione, but by King and Nord's method [5], i.e., the formulation of 2-methylthiophene and subsequent reduction. In its turn, 2-methylthiophene was prepared by the same method from thiophene. It was impossible to be certain that this method gave a pure compound and not a mixture of 2,5- and 2,3-dimethylthiophenes. In order to resolve this doubt we prepared a ketone by the action of acetyl chloride on the synthesized dimethylthiophene and a dinitro derivative by the method of Stetzkopf and coworkers [6]. The melting points of the latter and of the oxime of the former corresponded with data in the literature for 2,5-dimethyl-3,4-dinitrothiophene and the oxime of 2,5-dimethyl-3-(dinitro) methyl ketone, respectively. It was established in this way that the dimethylthiophene that we used was mainly, if not entirely, 2,5-dimethylthiophene.

In order to make sure that the bischloromethylidemethylthiophene of m.p. 68° that we obtained was indeed a tetrasubstituted thiophene having the properties of a bifunctional compound, we investigated some of its reactions. The compound was reduced with stannous chloride [7], the resulting substance of composition $C_8H_{12}S$ was not acetylated when treated with acetyl chloride in presence of stannous chloride and was identical in physical properties with the tetramethylthiophene described by Gaertner and Tonkyn [4]. When the substance of m.p. 68° was treated with benzene in presence of aluminum chloride, a compound was formed which corresponded in composition with 3,4-dibenzo-2,5-dimethylthiophene (V).



which we obtained also by the condensation of 2,5-dimethylthiophene with benzyl alcohol in presence of sulfuric acid [8]. These facts are in accord with the view that the substance of m.p. 68° is indeed a bifunctional derivative.

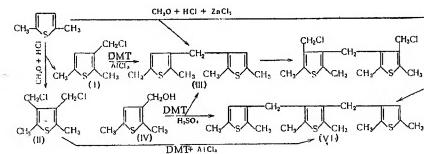
It was stated above that in chloromethylation experiments on 2,5-dimethylthiophene in the cold and at 50° we did not succeed in isolating a compound corresponding in composition to 3,3'-methylenebis[2,5-dimethylthiophene] (III). It must be pointed out here that Cagniant, who studied the chloromethylation of 2,5-dimethylthiophene [9] and 2-ethylthiophene [10] with chloromethyl methyl ether, states that the first of these compounds forms only a little, but the second quite a large amount, of the corresponding substituted methylenethiophene. Our experiments on the chloromethylation of 2,5-dimethylthiophene at 30° with formaldehyde, hydrochloric acid, and gaseous hydrogen chloride showed that, in this case also, only the bischloromethyl derivative is formed. Finally, it must be pointed out also that in the chloromethylation of 2,5-di-*tert*-butylthiophene in acetic acid*, formation of the corresponding derivative of 3,3'-methylenebithiophene was again not observed, only the bischloromethyl derivative being isolated.

A different picture is observed when 2,5-dimethylthiophene is chloromethylated in presence of zinc chloride. In this case two crystalline substances are formed, one corresponding in composition to (III) and the other to 3,4-bis(2,5-dimethyl-3-thienyl)-2,5-dimethylthiophene (VI):



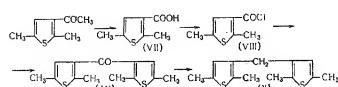
* The chloromethylation of 2,5-di-*tert*-butylthiophene was studied in our Laboratory by M. L. Kirmalova.

However, the first of these compounds differed in melting point (48.5°) from the compound described by Buu-Hoi and Nguen Hoan as 3,3'-methylenebis[2,5-dimethylthiophene], for which they obtained a melting point of 72°. This fact prompted us to seek other ways of preparing the compound (II), and the compound (VI) that accompanied it, with the object of making a comparison of properties. The scheme given below illustrates the results obtained:



in which DMT denotes 2,5-dimethylthiophene. From this scheme and the results given in the experimental part it will be seen that all of the methods selected for the preparation of the substituted methylenethiophenes (II) and (VI) give identical compounds. Since the structure of one of the starting materials, 2,5-dimethyl-3-thiophenemethanol was established by an independent method (see above), the structure (II) for the product of m.p. 48.5° may be considered to be established.

As, however, the causes of the nonidentity of the melting points of our preparation and previously described preparations of 3,3'-methylenebis[2,5-dimethylthiophene] still remained obscure, we decided to prepare it by yet another method, in accordance with the scheme:



The first three stages of this process have been described by Buu-Hoi and Nguen Hoan [11], and only the reduction of the ketone (IX) was carried out by us for the first time. We again obtained the compound of m.p. 48.5°, but at the same time we found some new discrepancies between constants observed by us and those given in the paper cited, namely those for the acid chloride (VII) and the ketone (IX). The causes of these and previously mentioned discrepancies are at present obscure.

EXPERIMENTAL

1. Chloromethylation of 2,5-Dimethylthiophene with the aid of Formaldehyde and Hydrogen Chloride. A mixture of 10 g of 2,5-dimethylthiophene, 50 ml of concentrated hydrochloric acid, and 14 ml of 37% formaldehyde was prepared in a flask cooled in an ice bath, and a powerful current of hydrogen chloride was passed in for one hour. The temperature of the mixture gradually rose to 16°. At the end of one hour the reaction mixture was poured into ice water and extracted several times with benzene. The benzene extract was washed with water and dried over magnesium sulfate. Benzene was distilled off, and the residue was vacuum-distilled (13 mm), the following fractions being collected:

Fraction I, b.p. 98-135°; 6.7 g; colorless liquid, darkening in color when kept
 Fraction II, b.p. 135-145°; 5.4 g; solid
 Fraction III, b.p. 145-205°; 0.4 g; solid
 Residue in flask 1.5 g

Refractionation of Fraction I gave 5.13 g of a substance boiling at 96-115° (13 mm) (the bulk of it came over at 98-102°). It was a colorless lachrymatory liquid, corresponding in analysis to the mono(chloromethyl) derivative. For the boiling point of 3-(chloromethyl)-2,5-dimethylthiophene the literature [3] gives 105-107° (20 mm).

Found %: C 52.65; H 5.74; Cl 5.54; 5.47
 C₆H₁₀Cl₂S. Calculated %: C 52.32; H 5.61

The solid b.p. 135-145° (13 mm) (Fraction II) was recrystallized from heptane. The colorless crystals obtained melted at 67-68° and did not change with keeping. There was no melting-point depression in a mixture test with the substance obtained by the chloromethylation of 2,5-dimethylthiophene by means of paraformaldehyde and hydrogen chloride at 50° (see below).

From Fraction III, b.p. 145-205° and the residue in the flask, a substance of m.p. 144-157° was obtained by crystallization from heptane. The same product, although with a sharper melting point, was isolated in another experiment carried out under the same conditions apart from the amount of formaldehyde taken, which was doubled. After being recrystallized from acetone and heptane, the substance melted at 172-173°, and there was no melting-point depression in a mixture test with the product obtained by the chloromethylation of 3,3'-methylenebis[2,5-dimethylthiophene] m.p. 48.5°.

Found %: C 54.30; 54.14; H 5.44; 5.46
 C₆H₁₀Cl₂S. Calculated %: C 54.05; H 5.40

2, 2, 5-Dimethyl-3-thiophenemethanol Acetic Ester. A mixture of 5.4 g of 3-(chloromethyl)-2,5-dimethylthiophene, 3 g of anhydrous sodium acetate, and 25 ml of glacial acetic acid was heated in a water bath at 60° for four hours. On the next day the precipitate of inorganic salt was filtered off and washed with acetic acid. Acetic acid was removed from the filtrate under reduced pressure, and water was added to the residue; the mixture was extracted several times with benzene. The combined benzene extracts of the reaction product were washed with water, benzene was distilled off, and the residue was vacuum-distilled. The product (3.8 g) was a colorless liquid, b.p. 125-128° (16 mm), n_D²⁰ 1.5120.

Found %: C 58.62; 58.83; H 6.44; 6.52; S 17.15; 17.18
 C₇H₁₀OS. Calculated %: C 58.69; H 6.52; S 17.40

3, 2, 5-Dimethyl-3-thiophenemethanol. 2,5-Dimethyl-3-thiophenemethanol acetic ester (3.7 g) was added to a solution of 0.02 g of sodium in 30 ml of absolute alcohol. The mixture was kept at room temperature for 48 hours, and the alcohol was then distilled off under reduced pressure. The residue was dissolved in 30 ml of absolute alcohol and the solution was evaporated under reduced pressure to small bulk; carbon dioxide was then passed through the solution until it was saturated. The precipitate was filtered off and alcohol was distilled from the filtrate. Water was added to the residue, and the mixture was extracted with benzene. Benzene was distilled off, and vacuum distillation of the residue gave 2.1 g of a colorless liquid, b.p. 112-113° (10 mm) and n_D²⁰ 1.5438, which became dark-colored on standing.

Found %: C 59.24; 59.44; H 6.87; 6.88; S 22.12
 C₇H₁₀OS. Calculated %: C 59.15; H 7.04; S 22.63

Urethan. A mixture of 0.7 g of the alcohol and 0.6 g of phenyl isocyanate was heated in a water bath for 45 minutes. When cool, the reaction product solidified; it was recrystallized, first from hexane and then from gasoline (b.p. 60-90°). After being dried in a vacuum the urethan melted at 76-76.5°, and there was no depression in melting point in a mixture test with the urethan obtained from the alcohol prepared by the reduction of 2,5-dimethyl-3-thiophenecarboxaldehyde. For the melting point of the urethan derived from 2,5-dimethyl-3-thiophenemethanol the literature [3] gives 77-78°.

Found %: C 64.03; 64.29; H 6.10; 5.97; S 12.23; 12.22; N 5.39
 C₁₄H₁₂NO₂S. Calculated %: C 64.37; H 5.75; S 12.26; N 5.35

4. Chloromethylation of 2,5-Dimethylthiophene with the aid of Paraformaldehyde and Hydrogen Chloride. A current of hydrogen chloride was passed through a mixture of 75 g of paraformaldehyde and 160 ml of concentrated hydrochloric acid at 50° until saturation was reached. Then - at the same temperature and with continued passage of a powerful current of hydrogen chloride - 27.5 g of 2,5-dimethylthiophene was added gradually to the mixture; when addition was complete the same reaction conditions were maintained for 90 minutes. When cool, the mixture was diluted with ice water. The reaction product was extracted several times with benzene. The benzene extract was washed with water, with 5% caustic potash solution, and again with water; it was then dried over calcium chloride. Benzene was distilled off, and the residue was vacuum-distilled. The bulk of the reaction product (41.2 g) came over at 130-142° (13 mm), the residue was vacuum-distilled.

Recrystallization from heptane gave 34.3 g of a colorless substance, m.p. 67-68.5°. Recrystallization from heptane and hexane, and also sublimation in a current of nitrogen, did not affect its melting point.

Found %: C 46.90; 46.86; H 5.02; 4.83; Cl 33.35; 33.87
 C₆H₁₀Cl₂S. Calculated %: C 45.93; H 4.78; Cl 33.97
 Found: M 202
 Calculated: M 209

3,4-Bischloromethyl-2,5-dimethylthiophene forms colorless crystals that remain unchanged in storage. It is soluble in benzene, ether, and acetone; less soluble in alcohol; sparingly soluble in cold heptane; and insoluble in water. It gives a precipitate of silver chloride with silver nitrate. 2,5-Dimethyl-3,4-thiophenedimethanol - which is obtained by the hydrolysis of its diisocyanate, which is itself prepared by the action of acetic acetate on 3,4-bischloromethyl-2,5-dimethylthiophene - is readily converted into 3,4-bischloromethyl-2,5-dimethylthiophene by shaking it with concentrated hydrochloric acid.

2,5-Dimethyl-3,4-thiophenedimethanol (0.8 g) was shaken with 8 ml of hydrochloric acid for 20 minutes. The mixture was then extracted with benzene. The benzene solution was washed, first with water, then with sodium bicarbonate solution, and then with water again. It was dried over magnesium sulfate. The benzene was distilled off, and 0.8 g of residue remained. It was dried over magnesium sulfate. The benzene was distilled off, and 0.8 g of residue remained. Recrystallization from heptane gave 0.5 g, m.p. 67-68°, un-depressed by admixture of 3,4-bischloromethyl-2,5-dimethylthiophene. Recrystallization of the 0.5 g from hexane gave 0.35 g, m.p. 67-68.5°.

5. Chloromethylation of 2,5-Dimethylthiophene with the aid of Chloromethyl Methyl Ether. A stirred mixture of 10 g of 2,5-dimethylthiophene, 14.4 g of chloromethyl methyl ether, and 30 ml of glacial acetic acid was maintained first at 0-10° for 30 minutes, and then at 23° for two hours. The reaction mixture was poured into ice water. The reaction product was extracted with benzene, and the extract was washed, first with water, then with saturated sodium bicarbonate solution, and then again with water. The solution was dried over magnesium sulfate, benzene was driven off, and the residue was vacuum-distilled; the following fractions being collected at 13 mm:

Fraction I, b.p. 96-98°; 7.6 g; colorless lachrymatory liquid
 Fraction II, b.p. 110-150°; 2.5 g; which partially solidified
 Fraction III, b.p. 155-184°; 1.2 g; a mixture of solid and oil
 Residue in flask 1.7 g

Refractionation of Fractions I and II gave 7.3 g of a substance of b.p. 96-100° (13 mm) and a small amount of a substance of m.p. 68.5-67.5° (after recrystallization from heptane). We did not succeed in isolating a pure product from Fraction III. The product of b.p. 96-100° (13 mm) was a colorless lachrymatory liquid that darkened when kept. It had n_D²⁰ 1.5462, and it was obtained in 51% yield.

6. Reaction between 3,4-Bischloromethyl-2,5-dimethylthiophene and 2,5-Dimethylthiophene in presence of Aluminum Chloride. A stirred mixture of 4.2 g of 3,4-bischloromethyl-2,5-dimethylthiophene, 5 g of 2,5-dimethylthiophene, 35 ml of carbon disulfide, and 0.2 g of aluminum chloride was maintained at room temperature for four hours and was then set aside overnight. On the next day carbon disulfide was distilled off, and water and benzene were added to the residue. The benzene layer was separated and washed, first with water, then with 5% sodium carbonate solution, and finally with water again. It was dried over magnesium sulfate. Benzene was distilled off, and 6.4 g of a solid residue was obtained which melted at 160-170° after recrystallization from heptane. When vacuum-distilled

(3-4 mm), the substance began to boil at about 200° and rapidly solidified in the side tube of the distilling flask. The product was dissolved in hot heptane, and on cooling the solution deposited colorless crystals, m.p. 174-175° (change began at 171°). A mixture test of these crystals with the substance of m.p. 174-175° obtained by the Friedel-Crafts condensation of 2,5-dimethylthiophene with 3-(chloromethyl)-2,5-dimethylthiophene showed no depression in melting point.

7. Condensation of 2,5-Dimethyl-3-thiophenemethanol with 2,5-Dimethylthiophene. A mixture of 2 g of 2,5-dimethylthiophene and 1.65 g of 2,5-dimethyl-3-thiophenemethanol was cooled with snow while addition was made of a mixture of equal weights of glacial acetic acid and concentrated sulfuric acid. The mixture was kept for two days at room temperature, and the reaction product, which had separated in the form of fine crystals, was filtered off. It was dissolved in hot heptane, and when the solution cooled 0.5 g of fine crystals separated. They were recrystallized from alcohol (the substance is sparingly soluble in hot alcohol), and they then melted at 170-175°. A mixture test with the substance of m.p. 174-175° obtained by reaction between 2,5-dimethylthiophene and 3-(chloromethyl)-2,5-dimethylthiophene in presence of aluminum-chloride showed no depression in melting point.

Found %: C 66.35; H 6.68; S 6.69
 $C_{10}H_{10}S_2$. Calculated %: C 66.66; H 6.67

In another experiment carried out under the same conditions we succeeded in isolating not only the above-described product, but also a small amount of a substance of m.p. 48°, which melted without depression when mixed with the substance of m.p. 48-49° isolated in the condensation reaction between 2,5-dimethylthiophene and 3-(chloromethyl)-2,5-dimethylthiophene.

8. Preparation of Substituted Methylenedithiophenes by the Friedel-Crafts Method. Aluminum chloride (0.2 g) was added to a mixture of 5.1 g of 2,5-dimethylthiophene, 7.3 g of 3-(chloromethyl)-2,5-dimethylthiophene, and 35 ml of carbon disulfide. The mixture was stirred for three hours at room temperature, and a further 0.3 g of aluminum chloride was added. On the next day the mixture was heated at 40-50° for 30 minutes. When cool, the aluminum salt was decomposed with ice water, the carbon disulfide layer was separated from the aqueous layer, and the aqueous layer was extracted several times with benzene. The combined carbon disulfide and benzene solutions were washed with water and dried over calcium chloride. The solvents were distilled off, and the residue, a solid, was recrystallized from heptane. The crystals obtained (2.8 g) melted at 150-158° (incipient liquefaction began below this temperature). The heptane mother liquor was evaporated to small bulk, when it was cooled, crystals (1.5 g) of m.p. 42-46° separated; when the filtrate was evaporated a further 1.5 g was obtained. The product of m.p. 42-46° was vacuum-distilled; it boiled at 150° (6 mm). After repeat recrystallization from alcohol the distilled product melted at 48-49.5°. The substance was soluble in benzene, acetone, ether, hot alcohol, and hot heptane, but insoluble in water.

Found %: C 66.23; H 6.41; S 26.82; 26.85
 $C_{10}H_{10}S_2$. Calculated %: C 66.10; H 6.77; S 27.1
 Found: M 238
 Calculated: M 236

The substance of m.p. 150-158° (2.8 g) (see above) was distilled at a residual pressure of 4 mm; it boiled at 195-207° and rapidly solidified in the side tube of the distilling flask, thus hindering distillation. After recrystallization from heptane the distilled product melted at 174-175° (change began at 172°).

Found %: C 66.74; H 6.59; S 26.29; 27.01
 $C_{10}H_{10}S_2$. Calculated %: C 66.68; H 6.67; S 26.66
 Found: M 351
 Calculated: M 360

The substance was soluble in ether and benzene, and it was sparingly soluble in heptane and hot alcohol.

9. Chloromethylation of 2,5-Dimethylthiophene with the aid of Formaldehyde and Concentrated Hydrochloric Acid in presence of Zinc Chloride. Over a period of 15 minutes, 4.5 g of 37% formaldehyde was dropped into an ice-cooled mixture of 11.2 g of 2,5-dimethylthiophene, 6 g of concentrated hydrochloric acid (sp. gr. 1.18), and 10 g of anhydrous zinc chloride;

the mixture was stirred mechanically at the same temperature for 45 minutes and then at 60° for three hours. When the mixture was cool, water, benzene, and ether were added. The organic layer was separated from the aqueous layer, and the latter was extracted several times with ether and benzene. The combined benzene-ether extracts were washed several times with water, and the solvents were distilled off under reduced pressure. The residue, which partially crystallized out, was diluted with a little ether. The part of the reaction product that did not dissolve in the ether was filtered off and washed several times with small amounts of ether (ether filtrate A), 3.1 g of a colorless crystalline substance, m.p. 150-164°, was obtained. After recrystallization from alcohol and then from heptane it melted at 165-170° (change began at 158°). The substance was distilled at a residual pressure of 4 mm; it came over at 205-215° and rapidly solidified in the side tube of the flask. After recrystallization from acetone the distilled product melted at 170-172.5° (incipient liquefaction began at 167°). A mixture with the substance obtained from 2,5-dimethylthiophene and its bischloromethyl derivative melted at 170-174°. Ether was distilled from the ether filtrate (A). The residue was distilled at a residual pressure of 10 mm and gave the following fractions:

Fraction I, b.p. 157-165°; 3.8 g
 Fraction II, b.p. 165-240°; 0.45 g
 Residue in flask 1.3 g

Fraction I (3.8 g) was redistilled. The product (3.5 g of crystals) came over at 134-135° (4 mm). After recrystallization from heptane it melted at 48.5° and there was no depression in melting point in a mixture test with the product of m.p. 48° isolated in the condensation of 2,5-dimethylthiophene with its mono(chloromethyl) derivative in presence of aluminum chloride.

Found %: C 66.03; H 6.07; S 27.11; 27.28
 $C_{10}H_{10}S_2$. Calculated %: C 66.10; H 6.77; S 27.11

10. Condensation of Benzyl Alcohol with 2,5-Dimethylthiophene. A mixture of 25 g of glacial acetic acid and 25 ml of concentrated sulfuric acid was added to an ice-cooled mixture of 5.6 g of 2,5-dimethylthiophene, 11 g of benzyl alcohol, and 50 ml of glacial acetic acid. The mixture was set aside for three days at room temperature and was then poured into ice water. The oil that separated was extracted with benzene. The benzene solution was washed with water, with 5% sodium carbonate solution, and then again with water. The benzene was distilled off, and vacuum distillation of the residue gave:

Fraction I, b.p. 60-120° (10 mm); 9.7 g
 Fraction II, b.p. 130-160° (5 mm); 2.4 g
 Fraction III, b.p. 160-190° (5 mm); 2.1 g

Fraction III was an immobile oil that partially crystallized out when kept in a refrigerator. The substance was dissolved in hot alcohol, and when the solution was cooled crystals of m.p. 68-69° (incipient melting at 67°) separated. In a mixture test with 3,4-dibenzyl-2,5-dimethylthiophene (see below) there was no depression of melting point.

11. Preparation of 3,4-Dibenzyl-2,5-dimethylthiophene. Anhydrous aluminum chloride (3.7 g) was added in small portions to a stirred ice-cooled solution of 5 g of the bischloromethyl derivative of m.p. 68° in 20 ml of dry benzene. After the addition of 10 ml of benzene, the mixture was set aside at room temperature, for several hours and then decomposed with water and hydrochloric acid. The benzene layer was separated, and the aqueous layer was extracted with benzene. The combined benzene solutions were washed with water and with sodium carbonate solution. The benzene was distilled off, and vacuum distillation of the residue - a dark-red liquid - gave:

Fraction I, b.p. 118-120° (5 mm); 0.46 g
 Fraction II, b.p. 187-191° (5 mm); 3 g (solid)
 Fraction III, b.p. 191-220° (5 mm); a small amount of red oil

Recrystallization of Fraction II from alcohol gave 1.9 g of colorless crystals, m.p. 68-69°, unchanged by further crystallization.

Found %: C 82.64; H 6.82; S 11.32; 11.13
 $C_{18}H_{26}S$. Calculated %: C 82.19; H 6.85; S 10.96

12. Chloromethylation of 2,5-Diethylthiophene. A powerful current of hydrogen chloride was passed into a mixture of 34 ml of 38% formaldehyde and 45 ml of concentrated hydrochloric acid until saturation was reached, and 2,5-diethylthiophene (10 g) was then added gradually at 30°. Hydrogen chloride was passed for a further two hours, and the mixture was then diluted with ice water and extracted with ether. The ether extract was washed with water and with a solution of sodium bicarbonate. It was dried over calcium chloride, ether was distilled off, and the residue was distilled at a residual pressure of 9 mm:

Fraction I, b.p. 128-134°, a small amount

Fraction II, b.p. 138-148°, 10.8 g (solid)

Recrystallization of Fraction II from heptane gave 6 g of a substance of m.p. 53°. The mother liquor yielded 2.6 g of a substance of m.p. 53-54°. After repeated recrystallization the melting point of the substance was 53-54°.

Found %: C 50.54; 50.67; H 5.86; S 5.75
 $C_{10}H_{14}Cl_2S$. Calculated %: C 50.63; H 5.91

3,4-Bischloromethyl-2,5-diethylthiophene is soluble in benzene and in hot alcohol; it is somewhat more difficultly soluble in heptane.

13. Chloromethylation of 2,4-Di-tert-butylthiophene. A mixture of 40 g of 37% formaldehyde, 20 ml of concentrated hydrochloric acid, and 100 ml of glacial acetic acid was saturated with hydrogen chloride gas, and 25.5 g of 2,4-di-tert-butylthiophene was then added gradually (over a period of 55 minutes) at 50-55°. After one hour at 50-55° and one hour at room temperature, the cooled mixture was poured into ice water. The reaction product separated in the form of crystals (39 g of crude product). The substance was found to be readily soluble in benzene, acetone, heptane, and hot acetic acid. After recrystallization from acetic acid, the substance melted at 86-86.5°. The yield of recrystallized product was 55%.

Found %: C 57.48; 57.46; H 7.29; 7.35

$C_{13}H_{18}Cl_2S$. Calculated %: C 57.34; H 7.51

No other individual products could be isolated in the chloromethylation of 2,5-di-tert-butylthiophene under the conditions described.

14. Reduction of 3,4-Bischloromethyl-2,5-dimethylthiophene. Stannous chloride (50 g) was mixed with 100 ml of acetic acid, and hydrogen chloride was passed to saturation, i.e., until the whole of the stannous chloride went into solution. The solution was filtered, and 10.4 g of the product of m.p. 68° obtained by the chloromethylation of 2,5-dimethylthiophene was added in small portions. The solution became slightly warm and gradually acquired a reddish-brown color. On the next day the mixture was poured into water, the greenish-yellow oil that separated was extracted with ether, and the extract was then shaken with caustic potash solution and with water. The extract was dried over calcium chloride and the ether was distilled off. Vacuum distillation of the residue gave 4.6 g of a substance having b.p. 75-78° (13-14 mm), n_D^{20} 1.5205.

Found %: C 68.69; 68.64; H 8.47; 8.53; S 22.46; 22.76

$C_9H_{12}S$. Calculated %: C 68.57; H 8.57; S 22.85

The product was unaffected by treatment with acetyl chloride in presence of stannic chloride.

15. Chloromethylation of 3,3'-Methylenebis[2,5-dimethylthiophene]. Freshly distilled chloromethyl methyl ether (6 g) was added to a cooled (ice water) solution of 3 g of the substance of m.p. 47-48° prepared by the chloromethylation of 2,5-dimethylthiophene with formaldehyde and hydrochloric acid in presence of zinc chloride. The mixture was heated for two hours in a water bath at 60°, and the crystalline precipitate formed was filtered off and washed with acetic acid. The crude product (4 g) melted at 167-168° (incipient melting at 155°). After being recrystallized from heptane the substance melted at 172.5-173°.

Found %: C 54.31; 54.46; H 5.26; 5.37

$C_{15}H_{18}S_2Cl_2$. Calculated %: C 54.05; H 5.40

16. Reduction of Bis(2,5-dimethyl-3-thienyl) Ketone. The following compounds were prepared by Buu-Hoi and Nguen Hoan's method: the acid (VII), m.p. 116-117° (from aqueous alcohol); the acid chloride (VIII), b.p. 103-105° (12 mm); and the ketone (IX), m.p. 63-64° (from alcohol). The ketone

(IX) was synthesized also by Hartough and Kosak's method [12], namely by the action of phosphoric oxide on a mixture of the acid (VII) and 2,5-dimethylthiophene; the ketone obtained again melted at 63°. In the paper referred to above [11] the following constants are given: for the acid (VII) m.p. 117-118°, for the acid chloride (VIII) b.p. 144-145° (13 mm), and for the ketone (IX) m.p. 79°.

The 2,5-dimethylthiophene that we used for the synthesis of the ketone was prepared from 2-methylthiophene by King and Nord's method [5]. The sample so obtained was distilled through a 17-plate column and had b.p. 136.5° (754 mm), n_D^{20} 1.6138, and d_4^{20} 0.9660.

In another experiment on the preparation of the ketone we took 2,5-dimethylthiophene that had been synthesized from 2,5-hexanedione and distilled through a 17-plate column (it had b.p. 136.9° (760 mm), n_D^{20} 1.5127, and d_4^{20} 0.9659). The bis(2,5-dimethyl-3-thienyl) ketone prepared from this material again melted at 63-63.5°.

Found %: C 62.11; 62.19; H 5.66; S 25.51; 25.53
 $C_{13}H_{14}OS_2$. Calculated %: C 62.40; H 5.60; S 25.60

Hydrazine hydrate (100%, 2.7 ml) was added to a mixture of 3.7 g of the ketone and 30 ml of diethylene glycol contained in a three-necked flask fitted with stirrer, reflux condenser, and thermometer. After 25 minutes at room temperature 3 g of caustic potash was added to the mixture, which was then heated for about one hour in a metal bath at 133-134°. A condenser set for distillation was then attached to the flask, and heating was continued until the temperature reached 198° (about two hours). The mixture was maintained at this temperature for three hours. When cool, it was diluted with ice water. The solid that then separated was filtered off, washed with water, and dried. Vacuum distillation of this gave 1.5 g of crystals, b.p. 172° (13 mm). Recrystallization of the product from alcohol gave 1.1 g of m.p. 47-48°, unaffected by repeated crystallization from alcohol. A mixture test of this substance with the substance of the same composition (m.p. 48°) obtained in a different way (see the first scheme, above) showed no depression in melting point.

SUMMARY

1. A study was made of the chloromethylation of 2,5-dimethylthiophene with a mixture of formaldehyde and hydrochloric acid and with chloromethyl methyl ether. The presence of the compound of m.p. 79° described by Buu-Hoi and Hoan could not be detected among the reaction products.

2. In the chloromethylation of 2,5-dimethylthiophene in presence of zinc chloride, compounds were formed which corresponded in composition to 3,3'-methylenebiphenyl, 2,5-dimethylthiophene and 3,4-bis(2,5-dimethyl-3-thienyl)-2,5-dimethylthiophene. These compounds were obtained also when 2,5-dimethylthiophene reacted with 3-chloromethyl-2,5-dimethylthiophene in presence of aluminum chloride and when 2,5-dimethylthiophene reacted with 2,5-dimethyl-3-thiophene methanol in presence of sulfuric acid.

3. The compound of m.p. 48.5° was obtained also by the reduction of bis(2,5-dimethyl-3-thienyl) ketone.

4. By the chloromethylation of 2,5-diethylthiophene and of 2,5-di-tert-butylthiophene under selected conditions, the corresponding dialkylbischloromethylthiophenes were obtained. The formation of substituted methyl-enedithiophenes was not observed under these conditions.

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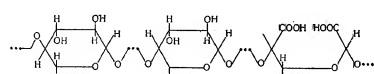
ION EXCHANGE ON CELLULOSE AND ITS DERIVATIVES

V. I. Ivanov and N. Ya. Lenshina

Celluloses, natural and isolated from plant tissues, are able to absorb cations from solutions of neutral salts. Various authors [1-5] have shown that, when cellulose is immersed in a salt solution, the solution becomes acid. Ion exchange on cellulose is now acquiring great theoretical and practical importance. Little progress has yet been made in the elucidation of the source of the exchange properties of cellulose. Some authors [4, 5] consider that ion exchange on cellulose results from the presence of inorganic substances (ash). Others [6, 7] consider that it results from the presence of noncellulosic components (pectic substances, etc.). It is coming to be considered that the exchange properties of cellulose are properties of the cellulose itself, and on this basis investigations are being made of celluloses that are free from inorganic cations and are capable of ion exchange. In a series of investigations it was shown [8] that the ion-exchange properties are dependent on the acidic nature of the cellulose; the authors consider that the acidic properties of cellulose may be intensified in the process of isolation from natural materials.

Sooke and Harris [9] investigated various samples of cotton cellulose, which were freed from inorganic substances or from pectic materials. Their investigations showed that, apart from the COOH groups belonging to pectic substances, cellulose itself contains COOH groups. They found that the exchange capacity of cellulose freed from inorganic substances was 0.066 mg.equiv./g., the capacity of cellulose freed from pectic substances was 0.011 mg.equiv./g., whereas the capacity of the original cellulose was 0.046 mg.equiv./g. Exchange attributable to cations of inorganic substances did not exceed 0.004 mg.equiv./g. Other authors [10, 11] state that COOH groups in oxidized celluloses react with multivalent cations with formation of salts of "cellulose acid". A series of papers [12-14] refer to the ion-exchange properties of oxidized celluloses. The availability of more precise chemical methods now enable the COOH content of cellulose to be determined. It has been found that the COOH content of cellulose prepared according to Corey and Gray is 0.004 mg.equiv./g., that of medicinal cotton wool is 0.02 mg.equiv./g. [8], and that of sulfate cellulose is 0.072 mg.equiv./g. [7].

No cellulose has yet been isolated which does not contain COOH groups. Analysis of the purest celluloses has shown that they contain 2-3 COOH groups per 1000 glucose residues [15]. If the COOH groups were to be found only in the residues of substances accompanying cellulose, as some authors think [6, 7], then they could not be concerned in the rapid change in the rate of the depolymerization of cellulose that occurs during the first few minutes of its treatment with acid solutions. It is therefore considered that these functional groups belong to particular units of the cellulose macromolecule. This can be expressed diagrammatically by the following formula [16]:



The dots indicate unchanged glucose residues (anhydro-D-glycose).

It has not been found possible to establish whether or not COOH groups are present in the molecule of cellulose before its isolation from the plant. Cellulose with which we have to deal in practice, and also cellulose intended for precise chemical investigations, will always contain functional groups other than OH groups and terminal CHO groups. The presence of COOH groups, even in very small amount, has a great effect on the properties of cellulose and of articles prepared from it. The question of the ash obtained from cellulose materials is important, for the presence of inorganic substances affects the viscosity, insulation properties, dyeability, etc., of cellulose [5, 6]. On the basis of this it may be supposed that ion exchange on cellulose free from inorganic ion-exchange cations occurs as a result of the presence of COOH groups. With the object of elucidating this matter we have begun an investigation on the ion-exchange properties of cotton cellulose and oxidized celluloses having various COOH contents. The COOH contents were determined by the calcium acetate method.

[17-19]. The solutions selected for trial were 0.005 M NiCl_2 and 0.005 M FeCl_3 . The solutions were passed through a column of cellulose (as cationite) at 3 ml per sec. per minute, the height of the column being 100 mm and its diameter 10 mm. The total exchange capacity was determined from the difference in cation concentration between the ingoing solution and the effluent. The process was continued until the cation concentration in the effluent was equal to that in the ingoing solution. The effluent was collected in 25 ml portions. The absorption of Ni^{2+} was carried out from a solution of pH 6.6, and that of Fe^{3+} was carried out from a solution of pH 1.4. In both cases absorption attained the value of the total exchange capacity. The experimental results for the absorption of Ni^{2+} and Fe^{3+} by cellulose and oxidized celluloses are given in the table; the values given being the means of groups of several determinations.

TABLE I
Absorption of Ni^{2+} and Fe^{3+} by Cotton Cellulose and Oxidized Celluloses

Cellulose preparation	COOH content (mg.equiv./100 g of sample)	Absorption of	
		Ni^{2+} (mg.equiv./100 g of sample)	Fe^{3+} (mg.equiv./100 g of sample)
Cotton cellulose	1.5	1.3	50
Oxidized cellulose			
1	56	53	43
2	220	200	53
3	280	215	46

As will be seen from the table, the absorption of Ni^{2+} from neutral solution can be correlated with the COOH content of the sample. The behavior of Fe^{3+} is quite different: the absorption is approximately the same for all of the samples, being about 50 mg.equiv./100 g. It follows that the absorption of Fe^{3+} by cellulose has a different mechanism than that of Ni^{2+} . The difference in the behavior of Fe^{3+} is of general interest in relation to the elucidation of the mechanism by which metal hydroxides are absorbed by cellulose.

Since ion exchange on cellulose occurs in many processes and affects the properties of cellulose and of articles prepared from it, we have undertaken a more detailed study of the matter. Cellulose is extensively applied also in chromatography. In addition to the separation of amines, amino acids, and other organic substances by the methods of partition chromatography, the separation of these substances by ion-exchange methods now finds application [20-23]. The study of ion exchange will throw new light on problems in chromatography on cellulose and its derivatives, and it will also enable us to determine the dependence of the properties of cellulose on the presence in it of various cations. Work in this field is continuing.

SUMMARY

- [1] Ion exchange on cellulose free from inorganic ion-exchange cations is the result of the presence of COOH groups.
- [2] The mechanism of the absorption of Fe^{3+} ions by cellulose is different from that of the absorption of Ni^{2+} ions.

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ORGANOBORON COMPOUNDS

COMMUNICATION 9. ACTION OF PHOSPHORUS PENTACHLORIDE ON
DIALKYLBORINIC AND ALKANECHBORONIC ESTERS. SYNTHESIS OF
DIALKYLCHLOROBORINES AND ALKANECHLOROBORONIC ESTERS

B. M. Mikhailov and T. A. Shchegoleva

Dialkylboric esters react with phosphorus pentachloride with formation of dialkylchloroborines (dialkylborinic chlorides), alkyl halides, and phosphoryl chloride:

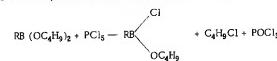


By this method butyl dibutylborinate was converted into dibutylchloroborine ($C_4H_9_2BCl$), and butyl butylpropylborinate was converted into chlorobutylpropylborine:



Dibutylchloroborine has been prepared previously by the action of hydrogen chloride on tributylborine [1]. Compounds of this type containing two different alkyl radicals have not been described previously.

Alkaneboronic esters react equally smoothly with phosphorus pentachloride, and, when one equivalent of phosphorus pentachloride is used, alkanechloroboronic esters are obtained in accordance with the equation:



In this way we prepared butyl esters of 1-butanechloroboronic and 1-propanechloroboronic acids, these being the first representatives of a new type of compounds in which boron is attached simultaneously with an alkyl group, an alkoxy group, and a chlorine atom.

EXPERIMENTAL

All operations were carried out in a nitrogen atmosphere.

Dibutylchloroborine. Phosphorus pentachloride (17.6 g) was added in portions to butyl dibutylborinate (16.8 g) contained in a three-necked flask fitted with an entry tube for nitrogen and a reflux condenser. When the exothermic reaction was complete, butyl chloride and phosphoryl chloride were distilled off under reduced pressure and were collected in a receiver cooled with solid carbon dioxide. The residue was then distilled and yielded 12 g (89%) of dibutylchloroborine, b.p., 58-60° (12 mm). After redistillation the substance boiled at

59.5–60° (12 mm) and 172–174° (atmospheric pressure). The literature [1] gives b.p. 173° and d_4^{20} 0.8590. The substance bursts into flame in the air.

Found %: B 6.75; Cl 22.53

$C_8H_{10}BCl$. Calculated %: B 6.74; Cl 22.09

The butyl chloride and phosphoryl chloride were also isolated.

Butylchloropyrophosphine. The procedure was similar to that of the preceding experiment. Reaction was between 13.3 g of butyl butylpropylborinate [2] and 15 g of phosphorus pentachloride. The product, amounting to 5.1 g (50%), was butylchloropyrophosphine, b.p. 57–61° (28 mm). After being redistilled it had b.p. 60–61° (28 mm) and d_4^{20} 0.8503. The substance bursts into flame in the air.

Found %: B 7.27; Cl 24.55

$C_7H_{10}BCl$. Calculated %: B 7.39; Cl 24.21

The butyl chloride and phosphoryl chloride were also isolated.

Butyl 1-Butanechboroate. The procedure was similar to that of the preceding experiment. Reaction was between 20.2 g of dibutyl 1-butaneborane and 19.0 g of phosphorus pentachloride. The product, amounting to 12.8 g (78%), was butyl 1-butanechboroate, b.p. 68–70° (13 mm). After being redistilled it boiled at 64–65° (10 mm) and had d_4^{20} 0.9025.

Found %: B 6.27; Cl 20.03

$C_9H_{12}BOCl$. Calculated %: B 6.13; Cl 20.09

In addition, 8.5 g of butyl chloride and 8.7 g of phosphoryl chloride were isolated.

Dibutyl 1-Propaneboronate. An ethereal solution of propylmagnesium chloride prepared from 36 g of magnesium, 116 g of propyl chloride, and 600 ml of ether was added at –70° to a solution of 160 g of trimethyl borate in 400 ml of ether. The reaction mixture was decomposed with 10% hydrochloric acid, and solvent was distilled from the ether layer. Butyl alcohol (400 ml) was added to the residue. Distillation removed the azeotropic mixture of butyl alcohol and water and then the remainder of the butyl alcohol, and the residue was then fractionally distilled. The product, amount to 132 g (44%), was dibutyl 1-propaneboronate, b.p. 86–90° (10 mm). After being redistilled the ester had b.p. 82–83° (7 mm) and d_4^{20} 0.8152.

Found %: B 5.57

$C_{11}H_{20}BOCl$. Calculated %: B 5.41

Butyl 1-Propanehchloroborate. The procedure was similar to that of the first experiment. Reaction was between 20.7 g of dibutyl 1-propaneboronate and 21.0 g of phosphorus pentachloride. The product, amounting to 14 g (63%), was butyl 1-propanehchloroborate, b.p. 59–67° (25 mm). After being redistilled it had b.p. 60–61° (22 mm) and d_4^{20} 0.8999.

Found %: B 6.83; Cl 22.15

$C_7H_{10}BOCl$. Calculated %: B 6.66; Cl 21.82

The butyl chloride and phosphoryl chloride were also isolated.

SUMMARY

1. Dialkylborinic esters react with phosphorus pentachloride with formation of dialkylchloroborines.
2. Alkaneboronic esters react with phosphorus pentachloride with formation of alkanechloroboronic esters.

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TERTIARY ALKYL FLUORIDES AND ALKYLENE DIFLUORIDES IN ORGANOMAGNESIUM SYNTHESIS

A. D. Petrov, V. L. Sushchinsky, and M. P. Shebanova

It is known that alkyl fluorides either do not form Grignard reagents or form them in negligible yield, even if very severe conditions are used [1]. We recently condensed tertiary mono- and di-chloro compounds with halogen compounds of the allyl halide type in presence of magnesium, following Yarovsky's method [2]. We showed that, under the given conditions, even halogen compounds that were unable to form Grignard reagents owing to peculiarities in the structure of their radicals entered into the condensation reaction with formation of olefins, although the yields were generally low. Taking into consideration the fact that the C–F bond energy (102 cal/mole) is considerably higher than the C–Cl bond energy (77.9 cal/mole), we decided to study the condensation reaction of tertiary alkyl fluorides and alkylenes difluorides whose chlorine analogs had already been investigated. The results, which are shown in Table 1, indicate that our calculations were justified and that the replacement of chlorine by fluorine in alkyl and alkylenes chlorides raised the yield by a factor of 2.5–3. Reaction with the monofluoro compounds was carried out in boiling ether, and reaction with difluoro compounds was carried out at –30°. In view of the high mobility of fluorine in alkyl fluorides [3], the fluoro compounds were prepared from olefins (and diolefins) and hydrogen fluoride at low temperature (–20 to –30°) and were not distilled, being used in the condensation with allyl halides in admixture with the original hydrocarbons.

The properties of the hydrocarbons obtained, together with values from the literature for comparison, are given in Table 2. It is interesting to note that high yields of hydrocarbons containing two quaternary carbons were attained as a result of the high energy of the C–F bond, which enabled the condensation reaction to be carried out rapidly both at +40° and at –30°. It is interesting to note also that, as a side reaction, diolefins are formed from difluoro compounds just as they are from dichloro compounds (this reaction was carried out at –20°) and from dibromo compounds (reaction proceeded only at +35°). In the last case it was not the dibromo compound that reacted, but a monobromo compound that had undergone allyl rearrangement.

EXPERIMENTAL

The hydrofluorination of the olefins (and diolefins) was carried out in a copper reactor fitted with stirrer, thermometer, and copper reflux condenser, through the upper open end of which dry ice and acetone were added. The reactor was placed in a cooling mixture maintained at –40°. Liquid anhydrous hydrogen fluoride was poured into the cooled reactor. The olefin (or diolefin) was then introduced from a dropping funnel and then through the condenser at such a rate that the temperature of the reaction mixture did not exceed –30° (the temperature in the condenser jacket was kept at –25°). When reaction was complete, the excess of hydrogen fluoride was removed with a current of nitrogen at 0–10°. Analysis for fluorine showed that the yields of tertiary monofluoro compounds varied from 30 to 60% and the yield of the difluoro compound was 22%. A difluoro compound was obtained from the diolefin corresponding to the pinacol from the branched ketone isobutyl methyl ketone in a yield of only 10%, but the corresponding dichloro compound could not be obtained at all. The unflattened fluoro compounds in admixture with the original hydrocarbons and the second component of the synthesis was added to magnesium in ether under the usual conditions of the Yarovsky procedure at the temperatures indicated above. The reaction products were decomposed in the usual way and then fractionated. The diolefin (VI) was oxidized with 3% potassium permanganate, and formic acid and 3,4-diethyl-3,4-dimethylhexanedioic acid were identified among the products.

TABLE 1

Formula of alkyl or allylene fluoride	Reagent	Reaction product	Yield (%)	Yield analogous dihalogencomp. Lit. reference
$\text{CH}_3 \text{CH}_2$ $\text{CH}_2=\text{C}-\text{CH}_2-\text{F}$ $\text{CH}_3 \text{CH}_3$	Mg^+ $\text{C}_2\text{H}_5\text{CH}_2\text{CH}_2 + \text{CH}_2$	CH_2CH_3 $\text{CH}_2-\text{O}-\text{C}-\text{CH}_2-\text{CH}=\text{CH}_2$ (I) CH_2CH_3	10.3 [4.5]	
CH_3 $\text{CH}_2-\text{CH}-\text{CH}_2-\text{C}-\text{F}$ CH_3	Mg	CH_2CH_3 $\text{CH}_2-\text{CH}-\text{CH}_2-\text{C}-\text{C}-\text{CH}_2-\text{CH}=\text{CH}_2$ CH_3 CH_2CH_3 CH_2CH_3 (II)	18 [6]	
CH_3 $\text{CH}_2-\text{CH}-\text{CH}_2-\text{C}-\text{F}$ CH_3	$\text{CIMgCH}_2-\text{CH}_2-\text{CH}_2$	CH_3 $\text{CH}_2-\text{CH}-\text{CH}_2-\text{C}-\text{C}-\text{CH}_2-\text{CH}=\text{CH}_2$ CH_3 CH_2CH_3 (III)	24 [8]	
CH_3CH_2 $\text{CH}_2-\text{C}-\text{C}-\text{F}$ CH_3CH_2 CH_3	$\text{Mg} + \text{CICH}_2-\text{O}-\text{CH}_2$ CH_3	CH_3 $\text{CH}_2-\text{C}-\text{CH}_2-\text{C}-\text{CH}_2-\text{CH}=\text{CH}_2$ CH_3 $\text{C}-\text{CH}_2$ CH_2CH_3 (IV)	42 [20]	[5]
CH_3CH_2 $\text{CH}_2-\text{C}-\text{C}-\text{CH}_2-\text{CH}_2$ CH_3	Mg^+ $\text{C}_2\text{H}_5\text{CH}_2-\text{CH}_2$	CH_3 $\text{CH}_2-\text{CH}-\text{CH}_2-\text{C}-\text{CH}_2-\text{CH}=\text{CH}_2$ CH_3 CH_2CH_3 (V)	36.4	
	Mg^+ $\text{C}_2\text{H}_5\text{CH}_2-\text{CH}_2$	CH_3 $\text{CH}_2-\text{CH}-\text{CH}_2-\text{C}-\text{CH}_2-\text{CH}=\text{CH}_2$ CH_3 CH_2CH_3 (VI)	37	[6]

TABLE 2

Hydrocarbon	Found		Calculated		Properties		B.p. (°C) (mm)	
	% C	% H	% C	% H	Literature reference	n_D^{20}	d_4^{20}	
(I)	85.76	14.43	85.62	14.38	156.3 (745) 157.5-158.5	1.4311 1.4308	0.7706 0.7711	[4]
(II)	84.90	15.01	84.84	15.16	218 (750)	1.4406	0.7904	
(III)	—	—	—	—	151 (745) 151-152	1.4156 1.4443	0.7390 0.7346	[7]
(IV)	85.73	14.40	85.62	14.38	81 (9) 72-73 (6)	1.4526 1.4528	0.8006 0.8055	[5]
(V)	85.21	14.51	85.62	14.38	175 (750)	1.4396	0.7694	
(VI)	86.23	14.04	86.6	13.4	149 (145) 210 (760)	1.4625 1.4620	0.8205 0.818	[6]

Found %: Ag 48.08; C 62.46; H 10.25
 $\text{C}_{12}\text{H}_{10}\text{O}_2$. Calculated %: Ag 48.64; C 62.61; H 9.57

The properties of 3,4-dibromo-3,4-dimethylhexane, obtained by the action of HBr on the corresponding diolefin were: b.p. 85-87° (5 mm); n_D^{20} 1.5060; d_4^{20} 1.387.

Found %: Br 58.76; C 36.60; H 5.98
 $\text{C}_9\text{H}_8\text{Br}_2$. Calculated %: Br 58.82; C 35.04; H 5.84

When the condensation product obtained from this dibromo compound and excess of allyl chloride was fractionated, only a diolefin of composition $\text{C}_{11}\text{H}_{10}$ was isolated; b.p. 176-178° (750 mm); n_D^{20} 1.4530; d_4^{20} 0.8002.

Found %: C 86.47; H 13.17
 $\text{C}_{11}\text{H}_{10}$. Calculated %: C 86.84; H 13.15

The following substances were identified among the oxidation products of this hydrocarbon: 2-butanoic acid, formic acid, and 2-methyllevulinic acid. This shows that the diolefin is 4,5,6-trimethyl-1,5-octadiene, which has been prepared previously [6].

SUMMARY

It was shown that, when chlorine is replaced by fluorine in tertiary alkyl halides and allylene dihalides, the yield in the condensation of these substances with Grignard reagents is increased by a factor of 2.5-3.

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* T.P. = C. B. Translation pagination.

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